

A Density Functional Theory Study of Adsorption and Decomposition of Nitroamine Molecules on the Al(111) Surface

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The density functional theory generalized gradient approximation has been used to study the adsorption of nitroamine molecules on the Al(111) surface. The calculations employ a 4×4 aluminum slab with three layers and three-dimensional periodic boundary conditions. There exist both physical and chemical adsorptions associated with different NH_2NO_2 molecule orientations and particular aluminum surface sites. For the nondissociative adsorption, the nitro oxygen atom orients to the Al surface. In the case of dissociative chemisorption, the O and N atoms bind with the Al surface. The O and N atoms of broken down N–O and N–N bonds form strong Al–O and Al–N bonds with the neighboring Al sites around the dissociation sites. Moreover, the radical species obtained as a result of N–O and N–N bond dissociation remains bonded to the surface. The largest adsorption energy is -893.8 kJ/mol. For the dissociation adsorption configurations, a significant charge transfer occurs. The most charge transfer is 3.04 e from the Al surface to the NH_2NO_2 molecule. The change of the electronic structures is obvious due to the dissociation of the N–O and N–N bonds and the formation of strong Al–O and Al–N bonds. It can be inferred that the aluminum surface is readily oxidized by the adsorbate of nitroamine, by dissociation of either the O and N atoms from the nitro group or the N atom from the amino group.

1. Introduction

Aluminum (Al) powder is the most commonly used metallic additive to explosives, propellants, and pyrotechnic compositions to improve the performance of high energetic materials. Al is known to add energy to the burning reaction in propellants and to enhance the blast effect of explosives and their underwater performance. Because of its large surface area, Al nanopowder can produce dramatic improvements in the performance of some energetic materials. The incorporation of Al nanopowder in propellants results in an increase in the burn rate.^{1–4} Some researchers have reported enhancements in detonation properties using Al nanopowders.^{1–7} In addition, Queenie et al. reported the effects of Al nanopowders on the thermal stability of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), castable mixtures of RDX and TNT (composition B), and ammonium perchlorate (AP).⁸ They also investigated the electrostatic discharge (ESD) sensitivity for the mixtures of Al with TNT, RDX, and AP.⁸

An important performance issue, particularly for nanoscale Al powders, is the formation of an Al oxide overcoat prior to combustion, which inhibits efficient burning. When the thickness of the oxide overcoat is large, its presence severely reduces the potential advantages of using ultrafine Al particles with such a high surface area-to-volume ratio. Consequently, identification of new methods for the passivation of Al particles to reduce the size of the oxide layer, without incurring a significant

decrease in performance, is being considered. Furthermore, Al is commonly used in formulations of propellants and explosives,⁹ and it is important to understand its reactions with energetic molecules. Currently, no experimental evidence is available to study the efficiency of passivation of Al nanoparticles when coated with various energetic materials. Moreover, a clear mechanism to describe the interaction of energetic materials (nitro compounds in particular) with Al surfaces is lacking. Available literature is the adsorption of nitromethane and FOX-7 molecules on the Al(111) surface.¹⁰ To understand some of the fundamental issues related to the role of energetic materials when deposited on an Al surface, our work focuses on the atomic level description of the interactions between the energetic compound of nitroamine and the Al(111) surface. Specifically, density functional theory (DFT) calculations are used to study the chemisorption properties of the nitro-containing compounds of interest for energetic materials applications on Al surfaces. Johnson considered that exposed surfaces of face-centered cubic (fcc) or closed-packed hexagonal metals are the (111) surface.¹¹ What's more, the dissociation and chemical corrosion easily take place on the (111) surface.¹² Therefore, this surface is a hot topic for chemical model investigations for the researchers.

This paper is organized as follows. A brief description of our computational method is given in section 2. The results and discussion are presented in section 3, followed by a summary of the main conclusions in section 4.

2. Computational Method

The calculations described in this paper have been performed using the CASTEP package¹³ with Vanderbilt type ultrasoft

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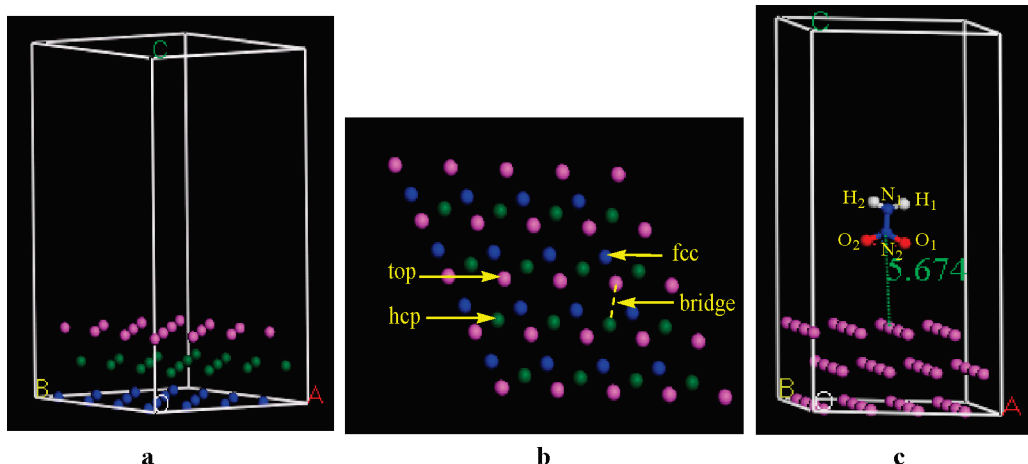


Figure 1. (a) Lateral view of the slab model of Al(111). Atoms in different layers are colored differently for easy identification. (b) Top view of the surface. Surface sites are depicted in the panel. (c) NH₂NO₂ molecule on the Al surface with no interactions.

pseudopotentials¹⁴ and a plane-wave expansion of the wave functions. Exchange and correlation were treated with the generalized gradient approximation, using the functional form of Perdew, Burke, and Enzerh (PBE).¹⁵ The electronic wave functions were obtained by a density-mixing scheme,¹⁶ and the structures were relaxed using the Broyden, Fletcher, Goldfarb, and Shannon (BFGS) method.¹⁷ The cutoff energy of the plane waves was set to 300.0 eV. Brillouin zone sampling was performed using the Monkhost–Pack scheme. The values of the kinetic energy cutoff and the k -point grid were determined to ensure the convergence of total energies.

The Al surface was represented by a slab model with periodic boundary conditions. Particularly, a 4×4 supercell with three layers containing 48 Al atoms was used to study the adsorption of the molecular systems. The slabs were separated by 18 Å of vacuum along the c -axis direction for the case with a nitroamine molecule. The cell size with a rhombic box of $a \times b \times c$ is $11.45 \text{ Å} \times 11.45 \text{ Å} \times 22.67 \text{ Å}$. In calculations of molecular adsorption on the surface, we have relaxed all of the atomic positions of the molecule, as well as the Al atoms located in the upper two layers of the slab.

Several tests have been performed to verify the accuracy of the method when applied to bulk Al and to the isolated NH₂NO₂ molecule, such as the optimum cutoff energy for calculations. For bulk Al, we have tested for convergence, using the k -point sampling density and the kinetic energy cutoff. In these calculations, a Monkhorst–Pack scheme with mesh parameters of $12 \times 12 \times 12$ has been used, leading to 56 k -points in the irreducible Brillouin zone. To determine the equilibrium bulk parameters of Al, we have uniformly scaled the lattice vectors and performed energy calculations as a function of the unit cell volume. The calculated lattice constants are the same values of 4.050 Å at $E_{\text{cut}} = 300 \text{ eV}$ and $E_{\text{cut}} = 400 \text{ eV}$. It can be concluded that at $E_{\text{cut}} = 300 \text{ eV}$, the bulk structure is well-converged with respect to the cutoff energy. The calculated lattice constant of 4.050 Å is also identical to the experimental value,¹⁸ indicating that the present set of pseudopotentials is able to provide a very good representation of the structural properties of bulk Al.

An equally good representation has been observed for the geometric parameters of the isolated NH₂NO₂ molecules. For example, on the basis of optimizations of the isolated NH₂NO₂ molecule in a rhombic box with dimensions of $11.45 \text{ Å} \times 11.45 \text{ Å} \times 22.67 \text{ Å}$, we obtained the following: equilibrium bond lengths of $r(\text{N–N}) = 1.399 \text{ Å}$, $r(\text{N–O}) = 1.250 \text{ Å}$, and $r(\text{N–H}) = 1.025 \text{ Å}$ and bond angles of $\theta(\text{H–N–H}) = 117.3^\circ$ and

$\theta(\text{O–N–O}) = 127.0^\circ$ at $E_{\text{cut}} = 300 \text{ eV}$. The increase of the cutoff energy to 400 eV leads to the following values: $r(\text{N–N}) = 1.396 \text{ Å}$, $r(\text{N–O}) = 1.250 \text{ Å}$, $r(\text{N–H}) = 1.025 \text{ Å}$, $\theta(\text{H–N–H}) = 118.0^\circ$, and $\theta(\text{O–N–O}) = 127.3^\circ$. We noticed that there are no significant differences between the values obtained at the two cutoff energies, indicating convergence of the results even at $E_{\text{cut}} = 300 \text{ eV}$. These values are also very similar to those calculated at the CCSD/cc-pVDZ theoretical level (N–N, 1.405 Å; N–O, 1.215 Å; N–H, 1.021 Å; H–N–H, 112.4° ; and O–N–O, 127.8°). In addition, the calculated values are also similar to the experimental data for gaseous NH₂NO₂ (N–N, $1.427 \pm 0.002 \text{ Å}$; N–O, 1.206 Å ; N–H, $1.005 \pm 0.01 \text{ Å}$; H–N–H, $115^\circ 11' \pm 2^\circ$; and O–N–O, $130^\circ 8' \pm 15'$).¹⁹ Our largest deviation of 0.044 Å is observed for N–O bonds.

The good agreement between our calculated properties of Al bulk and the isolated NH₂NO₂ molecule with the experiment and CCSD/cc-pVDZ theoretical predictions made us confident to proceed to the next step: the investigation of molecular adsorption on the Al(111) surface. This also suggests that the performed computational method is proper for the adsorption system of NH₂NO₂ molecule on the Al(111) surface.

For the case of chemical adsorption configurations, the corresponding adsorption energy (E_{ads}) was calculated according to the expression:

$$E_{\text{ads}} = E_{(\text{adsorbate}+\text{slab})} - E_{(\text{molecule}+\text{slab})} \quad (1)$$

where $E_{(\text{adsorbate}+\text{slab})}$ is the total energy of the adsorbate/slab system after the nitroamine molecule is adsorbed by the Al slab and $E_{(\text{molecule}+\text{slab})}$ is the single-point energy of the NH₂NO₂/slab system as a whole but without interactions between the nitroamine molecule and the Al slab (nitroamine molecule is as far as 5.7 Å away from the Al surface).

The $E_{(\text{adsorbate}+\text{slab})}$ and $E_{(\text{molecule}+\text{slab})}$ values were calculated with the same periodic boundary conditions and the same Brillouin zone sampling. A negative E_{ads} value corresponds to a stable adsorbate/slab system. Figure 1 shows the pictorial view of the Al slab model, the absorbed surface sites, and the configuration of the NH₂NO₂ molecule on the Al surface atoms with no interactions of adsorbate–Al.

3. Results and Discussion

The adsorption and decomposition of NH₂NO₂ molecule on the Al(111) surface are very complicated. There exist both

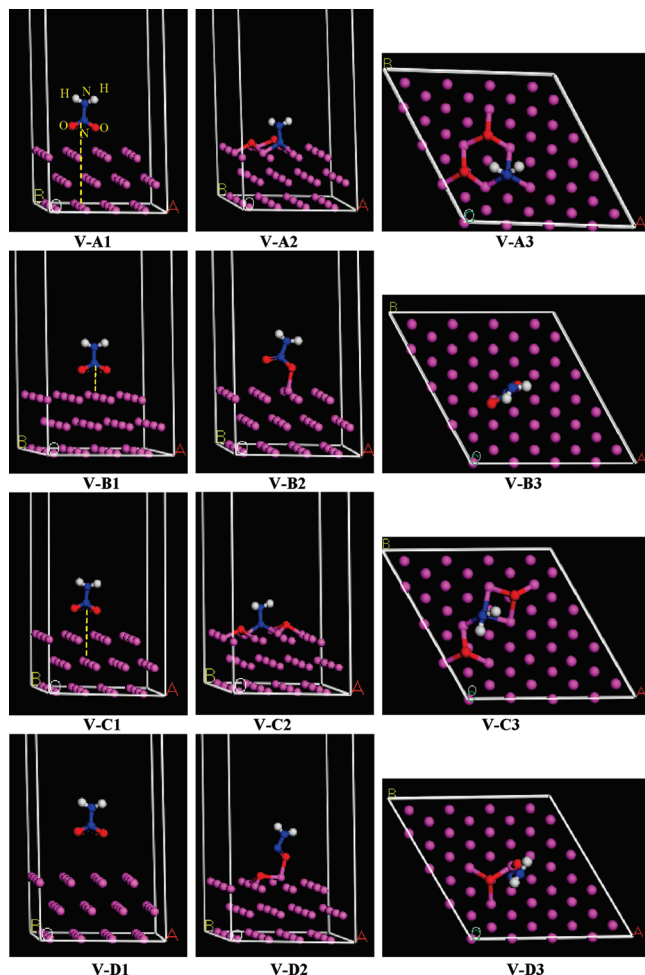


Figure 2. Adsorption configurations of nitroamine on the Al(111) surface obtained from the initial vertical configurations: V-A, V-B, V-C, and V-D denote the N atom above a fcc site, an on-top site, an hcp site, and a bridge site, respectively. Initial configurations are depicted in panels V-A1–V-D1, whereas the lateral and top views of the corresponding final configurations are shown in panels V-A2–V-D2 and V-A3–V-D3, respectively.

physical and chemical adsorptions, and the latter case results in the decomposition of the NH_2NO_2 molecule on the Al surface. There are five cases as follows:

- (1) The NH_2NO_2 molecule is nondissociative, for example, see Figure 2, V-B2.
- (2) $\text{NH}_2\text{NO}_2 \rightarrow \text{NH}_2\text{NO} + \text{O}$ (Figure 2, V-D2, and Figure 3, T-A2).
- (3) $\text{NH}_2\text{NO}_2 \rightarrow \text{NH}_2\text{N} + 2\text{O}$ (Figure 2, V-A2 and V-C2, and Figure 3, P-B2).
- (4) $\text{NH}_2\text{NO}_2 \rightarrow \text{NH}_2 + \text{NO} + \text{O}$ (Figure 3, P-A2).
- (5) $\text{NH}_2\text{NO}_2 \rightarrow \text{NH}_2 + \text{NO}_2$ (Figure 3, P-C2).

According to the orientation of the N–N bond relative to the Al(111) surface, V, P, and T denote vertical, parallel, and tilted adsorptions of NH_2NO_2 , respectively, as shown in Figures 2 and 3. For each configuration in Figures 2 and 3, three views are given. The first one, denoted with index 1, represents the initial configuration at the start of optimization process. The second and third ones, denoted with indices 2 and 3, respectively, represent lateral and top views of the optimized adsorption configuration after full relaxation of the atomic positions.

3.1. Geometries and Energies. The geometrical parameters are listed in Table 1. The adsorption energies are calculated by eq 1 and given in Table 2. As can be seen in Figure 2, the adsorption configurations of NH_2NO_2 were presented when the

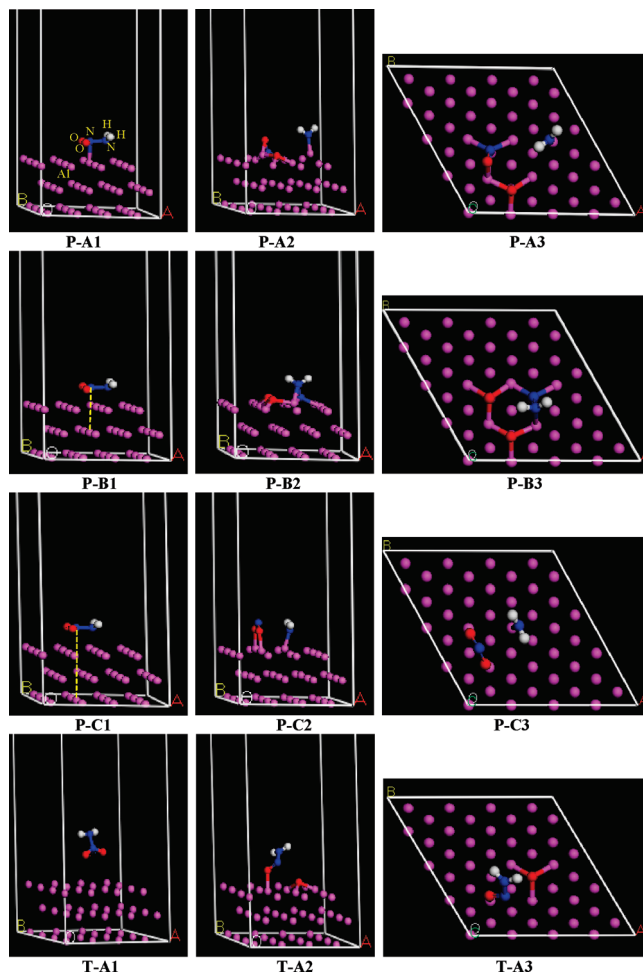


Figure 3. Adsorption configurations of nitroamine on the Al(111) surface obtained from initial parallel and tilted configurations: P-A, P-B, and P-C denote the N atom above an on-top site, an hcp site, and an fcc site from parallel configurations, respectively. T-A denotes the N atom above bridge sites from a tilted configuration. Initial configurations are depicted in panels P-A1–P-C1 and T-A1, whereas the lateral and top views of the corresponding final configurations are shown in panels P-A2–P-C2 and T-A2, P-A3–P-C3, and T-A3, respectively.

N–N bond was initially vertical to the Al surface, with the nitro group pointing down toward the Al surface. Configurations V-A1–V-A3 illustrate that the adsorption of NH_2NO_2 occurs at a fcc site. At this site, the adsorption leads to a complete dissociation of both O atoms of the nitro group. The NH_2N and two dissociated O atoms adsorb on the Al surface, resulting in a total six Al–O bonds and three Al–N bonds. The Al–O bonds and Al–N bonds are in the lengths of 1.843–1.887 and 1.930–1.969 Å, respectively. In addition, the N–H and N–N bonds are stretched to 1.034–1.035 and 1.477 Å, respectively, as compared to the initial values of 1.016 and 1.390 Å in Figure 1c (i.e., the NH_2NO_2 molecule is not interacting with the surface Al atoms).

V-B1–V-B3 of Figure 2 show that the N atom of the nitro group is above an on-top site of the Al atom. Adsorption at this site leads to the formation of a Al–O bond with a length of 1.940 Å. The distortion of the NH_2NO_2 molecule is small. As can be seen from Table 2, all of the bond angles and lengths change slightly except that a N–O bond length changes from 1.224 to 1.351 Å.

V-C1–V-C3 of Figure 2 illustrate the adsorption at a hexagonal closely packed (hcp) surface site. In this case, both O atoms of the nitro group dissociate, which is similar to V-A2.

TABLE 1: Geometrical Parameters of Equilibrium Adsorption of NH_2NO_2 on the Al(111) Surface^a

geometries	c^b	V-A2	V-B2	V-C2	V-D2	P-A2	P-B2	P-C2	T-A2
N ₁ –H ₁	1.016	1.034	1.029	1.033	1.029	1.026	1.032	1.028	1.032
N ₁ –H ₂	1.016	1.035	1.028	1.034	1.021	1.024	1.029	1.028	1.024
N ₁ –N ₂	1.390	1.477	1.392	1.470	1.345		1.497		1.351
N ₂ –O ₁	1.224		1.262			1.506		1.313	
N ₂ –O ₂	1.224		1.351		1.321			1.314	1.322
Al–O		1.843	1.940	1.768	1.846	1.784	1.844	1.910	1.865
		1.847		1.832	1.847	1.835	1.851	1.913	1.873
		1.863		1.856	1.852	1.843	1.855		1.876
		1.870		1.880	1.877	1.862	1.858		1.917
		1.878		1.899			1.858		
		1.887		1.901			1.873		
Al–N		1.930		1.857		1.813	1.916	1.838	
		1.944		1.989		1.895	1.925		
		1.969		2.015		1.896	1.955		
						1.972	2.065		
H–N–H	117	106	115	108	123	110	110	109	120
H–N–N	110	108	110	109	115/120		110		115/117
O–N–O	127		126					115	
O–N–N	116		113/120		109				109

^a Bond lengths are in Å, and bond angles are in degrees. ^b Isolated nitroamine molecule.

TABLE 2: Adsorption Energies (E_{ads}) and Adsorption Sites of NH_2NO_2 on the Al(111) Surface

relation of the N–N bond with the Al slab	configurations	adsorption sites	E_{ads} (kJ mol ^{−1})
vertical	V-A2	fcc	−788.6
	V-B2	top	−36.5
	V-C2	hcp	−756.8
	V-D2	bridge	−392.3
parallel	P-A2	top	−629.3
	P-B2	hcp	−893.8
	P-C2	fcc	−221.0
tilted	T-A2	bridge	−374.1

The N and dissociated O atoms interact strongly with the surface Al, which leads to the formation of six Al–O bonds and three Al–N bonds. The Al–O and Al–N bond lengths are in the range of 1.768–1.901 and 1.857–2.015 Å, respectively. The changes of the N–H and N–N bonds are also similar to V-A2.

Finally, V-D1–V-D3 of Figure 2 give the results of adsorption at the bridge site of the Al surface. Adsorption at this site leads to dissociation of one of the O atoms from nitro group. The dissociated and undissociated O atoms interact strongly with three neighboring Al atoms to form four Al–O bonds in lengths of 1.846–1.877 Å. The N–H bond lengths increase from 1.016 to 1.029 and 1.021 Å. The undissociated N–O bond is lengthened to 1.321 Å. However, the N–N bond length decreases from 1.390 to 1.345 Å.

In addition to the vertical adsorption configurations previously described, we have also tested the case in which the amino group of NH_2NO_2 initially oriented toward the Al surface. Chemisorption does not occur because the amino group does not interact with the surface Al atoms. Therefore, such configurations do not lead to stable adsorption and are not discussed further.

We have also studied the case in which the NH_2NO_2 molecule was initially parallel to the Al surface. Three cases have been investigated: the N atom of nitro group above an on-top site of an Al surface atom (P-A1 in Figure 3), above an hcp site (P-B1 in Figure 3), and above an fcc site (P-C1 in Figure 3). Our study indicated that the NH_2NO_2 molecule rotates to maximize the interaction with the Al surface during the optimization. As a result, the NH_2NO_2 molecule is dissociated in three ways, whose products are $\text{NH}_2 + \text{NO} + \text{O}$, $\text{NH}_2\text{N} + 2\text{O}$, and $\text{NH}_2 + \text{NO}_2$, respectively.

P-A1–P-A3 of Figure 3 illustrate the case in which the NH_2NO_2 molecule is dissociated into NH_2 , NO , and O . The products interact strongly with the surface Al atoms. Therefore, four Al–O bonds and four Al–N bonds are formed, with lengths of 1.784–1.862 and 1.813–1.972 Å, respectively. As compared to the isolated NH_2NO_2 molecule, both N–H bond lengths are stretched to 1.026 and 1.024 Å; the N–O bond length of NO is stretched to 1.506 Å due to the strong interaction of the N and O atoms with the surface Al atoms. The H–N–H angle decreases 7° because the N atom is adsorbed by an Al atom. It is deduced that these dissociated products are activated.

P-B1–P-B3 of Figure 3 give the results of adsorption on the Al surface, which at this site leads to complete dissociation of both O atoms of the nitro group. The products of the NH_2NO_2 molecule dissociated in P-B1–P-B3 are similar to those of V-A2 and V-C2. However, both N atoms in P-B2 interact with the surface Al atoms instead of only one N atom interacting with Al in V-A2 and V-C2. The Al–O and Al–N lengths are 1.844–1.873 and 1.916–2.065 Å, respectively. What's more, the elongations of the N–H and N–N bonds in P-B1–P-B3 are larger than those of V-A2 and V-C2. The corresponding adsorption energy is the highest of all adsorption energies, which is −893.8 kJ/mol.

P-C1–P-C3 of Figure 3 give the case in which the NH_2NO_2 molecule is dissociated to NH_2 and NO_2 . Both O atoms of NO_2 and N of NH_2 combine with Al atoms to form two Al–O bonds with lengths of 1.910 and 1.913 Å and an Al–N bond with length of 1.938 Å. Because of the interaction of NH_2 and NO_2 with the surface Al atoms, N–H and N–O bond lengths, which are 1.028 and 1.313/1.314 Å, respectively, are longer than the experimental and theoretical values for the isolated molecule. Additionally, the O–N–O and H–N–H angles are slightly smaller than those of the isolated molecule.^{20,21}

Finally, the case of T-A1–T-A3 was investigated in which the N–N of the NH_2NO_2 molecule is initially tilted to the Al surface and the N atom of the nitro group is above a bridge site of the first layer Al atoms. This adsorption is similar to V-D2, which also leads to dissociation of one of the O atoms from the nitro group. Four Al–O bonds are formed with lengths of 1.865–1.917 Å. The changes of geometrical structure on the NH_2NO (after another N–O bond rupture) are similar to those of V-D2.

TABLE 3: Atomic Charge (e) of Equilibrium Adsorption of NH_2NO_2 on the Al(111) Surface

atom	e^a	V-A2	V-B2	V-C2	V-D2	P-A2	P-B2	P-C2	T-A2
N ₁	-0.78	-0.79	-0.74	-0.79	-0.70	-1.26	-0.83	-1.20	-0.68
N ₂	0.53	-0.87	0.41	-0.87	0.03	-0.85	-0.92	0.21	0.03
O ₁	-0.37	-1.03	-0.38	-1.02	-1.02	-0.69	-1.02	-0.46	-0.99
O ₂	-0.37	-1.02	-0.49	-1.02	-0.52	-1.04	-1.04	-0.46	-0.50
H ₁	0.49	0.39	0.48	0.39	0.45	0.40	0.42	0.39	0.43
H ₂	0.49	0.39	0.49	0.39	0.50	0.39	0.43	0.39	0.49
Al linked two O atoms		0.88			0.89		0.86		
Al linked an O atom		0.47	0.37	0.50	0.47	0.46	0.46	0.34	0.45
				0.47	0.46	0.41	0.46	0.34	0.44
				0.44					0.40
									0.35
Al linked an O atom and a N atom		0.78		0.82		1.27 ^b	0.78		
		0.73		0.77			0.99 ^c		
				0.66					
Al linked a N atom		0.42				0.62	0.37	0.49	
						0.47			
						0.39			

^a Isolated nitroamine molecule. ^b Al links with two O atoms and a N atom. ^c Al links with an O atom and two N atoms.

As can be seen from Table 1 and Figures 2 and 3, when the NH_2NO_2 molecule is not dissociated, the corresponding adsorption energy is small, which is -36.5 kJ/mol. When the NH_2NO_2 molecule is dissociated, the corresponding adsorption energies are very large. The adsorption energies with both N–O bonds dissociated in V-A2 and V-C2 configurations are -788.6 and -756.8 kJ/mol. They are almost two times the adsorption energies of V-D2 or T-A2 (-392.3 and -374.1 kJ/mol, respectively). Although the decomposition products of P-B2 are the same as those of V-A2 and V-C2, the corresponding adsorption energies are much larger than those of V-A2 and V-C2, because there is an additional Al–N bond in P-B2 as compared to V-A2 and V-C2.

In addition, when the decomposition products of the NH_2NO_2 molecule in V-A2, V-C2, and P-B2 configurations are of three radical species ($\text{NH}_2\text{N} + 2\text{O}$), their adsorption energies are much larger than those of two radical species ($\text{NH}_2\text{NO} + \text{O}$ or $\text{NH}_2 + \text{NO}_2$). Herein, these radical species readily oxidize the Al and form strong Al–O and Al–N bonds.

In a word, the NH_2NO_2 molecule is decomposed to different products when initially being placed on different surface sites, resulting in strongly chemical adsorptions. In addition to the formation of strong Al–O bonds, the Al–N bonds are also formed through the strong interaction of N atoms in either the nitro group or the amino group with the surface Al atoms. The fact that the dissociation of the nitro group and the N–N bond on the Al(111) surface is observed in simple energy minimizations suggests that the uncoated Al surface is very active to the electron acceptors as further discussed below.

3.2. Charge Transfer. A useful tool to provide a quantitative measure of charge transfer is the Mulliken population analysis method,²² in which the electronic charge is distributed among the individual atoms. Table 3 gives atomic charges of equilibrium adsorption of the NH_2NO_2 molecule on the Al(111) surface. The obtained charges indicate that significant charge transfer occurs as a result of adsorption. For a nondissociative adsorption configuration, such as V-B2, the charge of 0.22 e is transferred from the surface Al atoms to the NH_2NO_2 molecule, as compared to the **c** configuration (Figure 1). The charges of N and O atoms decrease, while those of the surface Al atoms increase.

For N–O bond-dissociated adsorption configurations of V-D2 and T-A2, the charges of 1.25 and 1.21 e are transferred from the surface Al atoms to the adsorbate, respectively, as compared

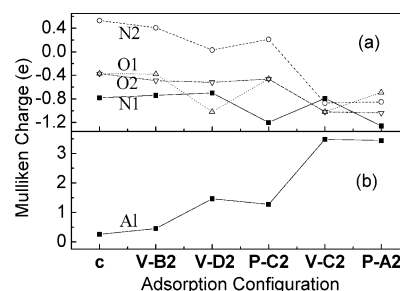


Figure 4. Mulliken charges on the individual N, O, and Al atoms. (a) Mulliken charges on each individual atom of nitroamine. Configuration **c** refers to Figure 1c in which there is no interaction between nitroamine and Al surface, V-B2 refers to nondissociative adsorption, V-D2 and P-C2 refer to dissociative adsorptions with one bond rupture of nitroamine, and V-C2 and P-A2 refer to dissociative adsorptions with two bond ruptures of nitroamine. (b) Mulliken charges on the top layer of Al.

to **c**. Similarly, for the results of both N–O bond-dissociated adsorption in V-A2, V-C2, and P-B2, the transfer charges are 2.92 , 2.91 , and 2.95 e, respectively.

For the configuration P-C2 of N–N bond-dissociated adsorption, the transfer charge is 1.12 e. Finally, in the case of a N–N bond and a N–O bond-dissociated adsorption for P-A2, the charge of 3.04 e is transferred from the surface Al atoms to the adsorbate, which is for all of the adsorption configurations.

Moreover, as can be seen from Figure 4a, for the adsorption configurations of the N–O bonds dissociated in V-D2 and V-C2, the charge on the amino N atom is almost unchanged in comparison with **c**. From **c** to V-B2, because O1 and amino N atoms do not bond with Al atoms, their charges are almost unchanged. However, the charge on the nitro N atom and O2 atom bonding with an Al atom decreases slightly. For V-D2, because of the dissociation of the N2–O1 bond and no dissociation of the N2–O2 bond, the charge on the N2 and O1 atoms bonding with the Al atoms decreases dramatically, but the charge on the O2 atom bonding with an Al atom is unchanged. From V-D2 to V-C2, because of the further dissociation of the N2–O2 bond and the formation of more Al–O and Al–N bonds, the charges of N2 and O2 atoms decrease obviously.

For P-C2, because of the dissociation of the N–N bond and the formation of an Al–N1 and two Al–O bonds, the charge on the

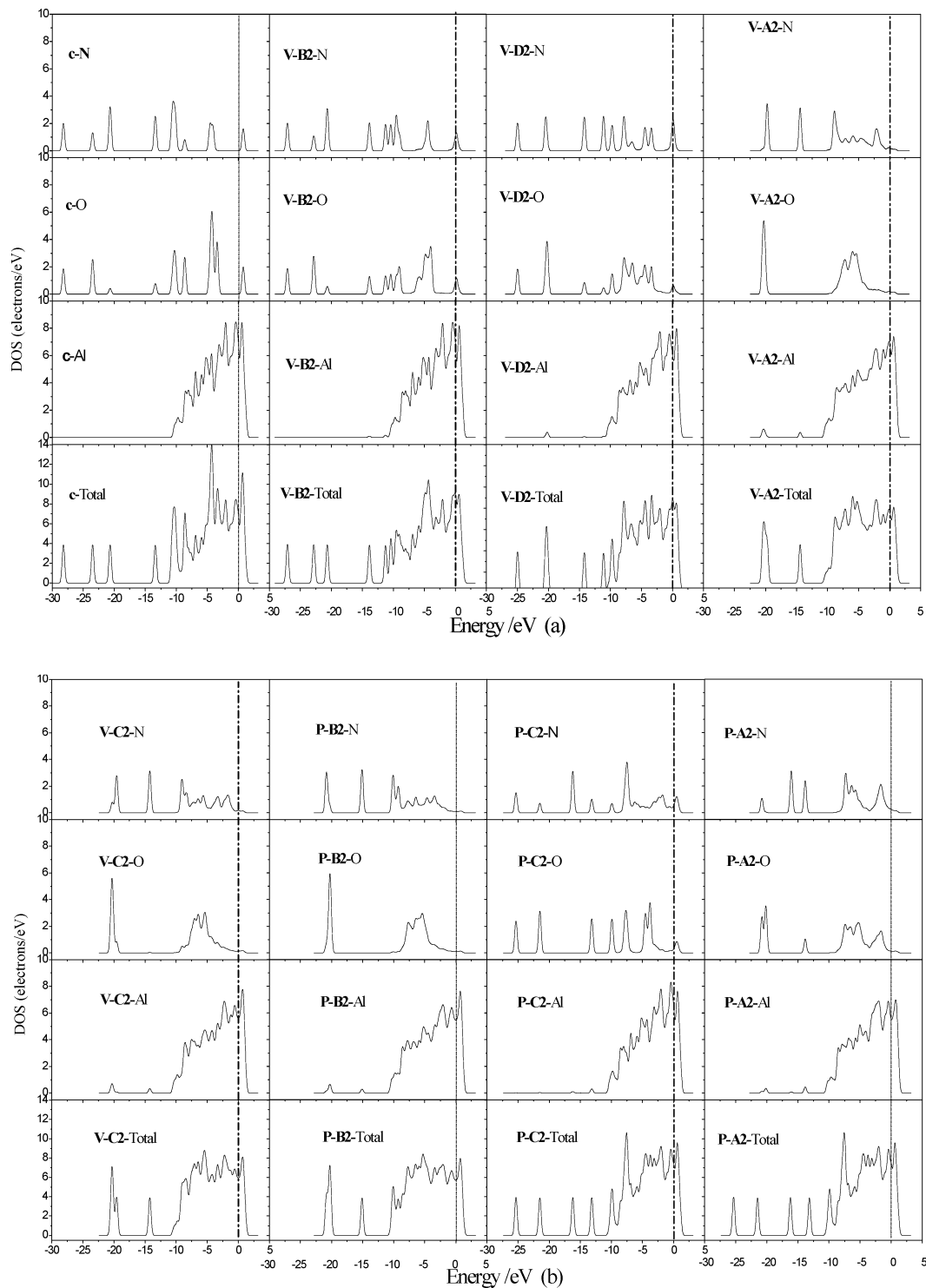


Figure 5. Total DOS and their projections on the N, O, and Al atoms for all adsorption configurations except for T-A2. Configuration **c** refers to Figure 1c.

N1 atom (i.e., amino N atom) decreases dramatically, whereas the charges on the N2 atom (i.e., nitro N atom) and two O atoms change slightly, and the charges of two O atoms are identical. From P-C2 to P-A2, with the further dissociation of the N2–O2 bond, charges of N2 and O2 atoms decrease sharply due to the formation of Al–N2 and more Al–O bonds. Figure 4b indicates that charges of the Al atoms increase with the number of the dissociated bonds on the NH_2NO_2 molecule increasing.

In a word, the charges on the nitro N atom of those are identical because the number on the dissociated bonds of V-C2

and P-A2 is equal, and the nitro N atom with three nearby surface Al atoms forms three almost identical Al–N bonds. The charges on two nitro O atoms of V-C2 and a nitro O atom (i.e., N–O dissociated O atom) of P-A2 are identical because each O atom combines with three nearby surface Al atoms and forms three almost identical Al–O bonds. With the number of the dissociated N–O and N–N bonds on NH_2NO_2 molecule increasing, the charges on N and O atoms decrease sharply.

3.3. The Density of States (DOS). The electronic structure is intimately related to their fundamental physical and chemical

properties. Moreover, the electronic structures and properties are related to the adsorptions and decompositions for the adsorbates. The discussion above suggests that the decomposition of the NH_2NO_2 molecule on the Al surface initiates from the rupture of N–O and N–N bonds and results in the formation of Al–O and Al–N bonds. Therefore, the knowledge of their electronic and properties appears to be useful for further understanding the behaviors of the NH_2NO_2 molecule on the Al surface.

Figure 5 displays the calculated total DOS and their projections on the N, O, and Al atoms for all adsorption configurations besides T-A2, since the DOS of T-A2 is similar to that of V-D2. Clearly, the total DOS equals the sum of its projections on N, O, and Al atoms for all adsorption configurations. The electronic structures vary with adsorption configurations due to the differently dissociated products of the NH_2NO_2 molecule.

As shown in Figure 5, for N and O atoms of V-B2, the highest peak values of DOS become smaller than those of **c**, whereas the number of DOS peaks becomes more than those of **c** in the range of -15 to 0 eV. However, the DOS of surface Al atoms appears almost unchanged, as compared to **c**. This indicates the weak interaction of the NH_2NO_2 molecule with the surface Al atoms.

For V-D2, the DOS of the O atom becomes smooth and broad in the range of -15 to 0 eV, while the peak number of DOS on the N atom becomes more, and the DOS of the Al atom appears as a small peak at the energy of -20 eV, in comparison with **c**. This suggests the dissociation of N–O bond and the formation of a strong Al–O bond. For P-C2, the change of the DOS of N atom is obvious in the range of -10 to 0 eV due to the N–N bond dissociated, while the change of the DOS on the O atom is small, which illustrates the N–O bond undissociated. For P-A2, the N and O atomic DOS peak numbers are further fewer than P-C2. The band energy of P-A2 becomes broad, and the individual peaks of DOS are overlapped. This illustrates the dissociation of both the N–N bond and an N–O bond.

For V-A2, V-C2, and P-B2, the changes in the DOS of N, O, and Al atoms are obviously similar to each other. In the range of -10 to 0 eV, the individual peaks of N and O atomic DOS are overlapped. However, at the other range, the peak number of the DOS on the N and O atoms becomes fewer than that of **c**. When bonding interactions between the adsorbates and the Al surface are strengthened, the DOS shifts and overlaps with respect to those of **c**. These explain the dissociation of N–O and N–N bonds and the formation of strong Al–O and Al–N bonds. The results also show the very strong interaction of the decomposition products from NH_2NO_2 with the surface Al atoms. In addition, the less the DOS peak number of N and O atoms is, the more the number of the formation of Al–O and Al–N bonds is.

5. Conclusion

The interactions of the nitroamine molecule with the Al(111) surface have been investigated on the basis of optimizations performed using plane-wave DFT and the PBE exchange-correlation functional. The major findings can be summarized as follows.

(1) The vertical, parallel, and tilted adsorption configurations were obtained by optimization. There exist both physical and chemical adsorptions when the nitroamine molecule approaches the Al surface. The NH_2NO_2 molecule is decomposed to four kinds of cases ($\text{NH}_2\text{NO} + \text{O}$, $\text{NH}_2\text{N} + 2\text{O}$, $\text{NH}_2 + \text{NO}_2$, and $\text{NH}_2 + \text{NO} + \text{O}$) due to the different NH_2NO_2 molecule orientations and different Al(111) surface sites. Fragments of

the NH_2NO_2 molecule decomposition are absorbed by the Al surface. The largest adsorption energy is -893.8 kJ/mol when the NH_2NO_2 molecule is parallel to the hcp sites of the Al surface, that is, P-B2 in Figure 3. The Al is readily oxidized by the O and N atoms of the dissociatively adsorbed nitroamine. The dissociations of the N–O and N–N bonds result in the formations of strong Al–O and Al–N bonds.

(2) The significant charge transfers occur for the dissociative adsorption configurations. The most charge transfer is 3.04 e from the Al surface to the NH_2NO_2 molecule for P-A2 in Figure 3. With the number of the dissociated bonds on the NH_2NO_2 molecule increasing, the charges on N and O atoms decrease sharply, while charges of the Al atoms increase. These large redistributions are consistent with the strong adsorption energies that compensate for the energies required by the N–O and N–N bond dissociations.

(3) In addition, the DOS projections on the N and O atoms for dissociated N–O and N–N bond adsorptions occur with an obvious shift of peaks, which infers that energy bands become broad and the interactions of chemical bonds are strengthened. For all adsorption configurations, the less the DOS peak number of N and O atoms is, the more the number of the newly formed Al–O and Al–N bonds is.

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