

**First Principles Calculations of the Adsorption of Nitromethane
and 1,1-Diamino-2,2-dinitroethylene (FOX-7) Molecules on
 $\text{Al}_2\text{O}_3(0001)$ Surface**

Dan C. Sorescu,* Jerry A. Boatz,** and Donald L. Thompson***

- * U. S. Department of Energy, National Energy Technology Laboratory,
P. O. Box 10940, Pittsburgh, PA 15236
- ** Air Force Research Laboratory, AFRL/PRSP, Edwards AFB, CA 93524
- *** Department of Chemistry, University of Missouri, Columbia, MO 65211

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE AUG 2004		2. REPORT TYPE		3. DATES COVERED -	
4. TITLE AND SUBTITLE First Principles Calculations of the Adsorption of Nitromethane and 1,1-Diamino-2,2-dinitroethylene (FOX-7) Molecules on Al₂O₃(0001) Surface				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Dan Sorescu; Jerry Boatz; Donald Thompson				5d. PROJECT NUMBER 2303	
				5e. TASK NUMBER M2C8	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC),AFRL/PRSP,10 E. Saturn Blvd.,Edwards AFB,CA,93524-7680				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT First-principles calculations based on density functional theory (DFT) and the generalized gradient approximation (GGA) have been used to study the adsorption of nitromethane (NM) and 1,1-diamino-2,2-dinitroethylene (FOX-7) molecules on the basal plane of an alpha-Al₂O₃ crystal. The calculations employ a (2x2) supercell slab model and 3D periodic boundary conditions. Based on these calculations we have determined that both NM and FOX-7 molecules can adsorb nondissociatively on the surface with the most stable adsorption configurations parallel to the surface. The binding energies are in the range 25.3-26.0 kcal/mol for NM and 35.6-48.3 kcal/mol for FOX-7 depending on the relative molecular orientation and the surface sites. The minimum energy pathways for NM dissociation have been determined and a low energy pathway leading to H-atom elimination with formation of adsorbed CH₂NO₂ and hydroxyl species has been identified. Additional calculations have focused on adsorption properties of aci-nitromethane tautomers and on description of the energetic pathways connecting adsorbed nitromethane molecule with these tautomers.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 53	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

ABSTRACT

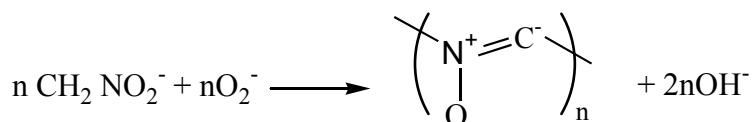
First-principles calculations based on density functional theory (DFT) and the generalized gradient approximation (GGA) have been used to study the adsorption of nitromethane (NM) and 1,1-diamino-2,2-dinitroethylene (FOX-7) molecules on the basal plane of an α -Al₂O₃ crystal. The calculations employ a (2x2) supercell slab model and 3D periodic boundary conditions. Based on these calculations we have determined that both NM and FOX-7 molecules can adsorb nondissociatively on the surface with the most stable adsorption configurations parallel to the surface. The binding energies are in the range 25.3-26.0 kcal/mol for NM and 35.6-48.3 kcal/mol for FOX-7 depending on the relative molecular orientation and the surface sites. The minimum energy pathways for NM dissociation have been determined and a low energy pathway leading to H-atom elimination with formation of adsorbed CH₂NO₂ and hydroxyl species has been identified. Additional calculations have focused on adsorption properties of *aci*-nitromethane tautomers and on description of the energetic pathways connecting adsorbed nitromethane molecule with these tautomers.

I. Introduction

The interaction of powderized aluminum with energetic materials represents a topic of significant interest as such materials can be used as energetic ingredients in rocket propellant formulations.¹ Its primary roles in energetic materials formulations include increasing the combustion exothermicity and the regression rate of solid propellant grains and enhancing the blasting effect of explosives.² Moreover, aluminum particles have been found to have beneficial effects by reducing the combustion instabilities in rocket motors.^{2,3} The efficiency of such processes to depend on the size of the Al particles. For example, in the case of Al nanopowders, significant improvements in the performance of some energetic materials over the common micron-size Al powders have been reported.^{4,5}

Besides energetic materials applications, the interaction of nitromethane with oxides has also attracted the interest of the catalysis community. Nitromethane has been considered as a prototypical compound whose study can help to elucidate the reaction mechanism of catalytic reduction of nitric oxides by hydrocarbons under oxygen-rich conditions.⁶⁻⁸ Yamaguchi⁶ has reported thermal decomposition studies of nitromethane (NM) adsorbed on γ -alumina, pretreated at 773 K, based on infrared spectroscopy, NMR spectroscopy and temperature-programmed desorption (TPD) measurements. He found that at room temperature NM adsorbs both molecularly (undissociated) in a weakly physisorbed state as well as in a dissociated state as *aci*-anion nitromethane (*aa*-NM, CH_2NO_2^-). It was suggested⁶ that *aa*-NM may be formed as a result of the interaction between NM and the oxide surface, with formation of a surface hydroxyl group via the reaction $\text{CH}_3\text{NO}_2 + \text{O}_2^- \rightarrow \text{CH}_2\text{NO}_2^- + \text{OH}^-$. The *aa*-NM species was found to remain stable on the surface up to $T = 373$ K. Above this temperature, two intermediate species

were formed by decomposition of the *aci*-anion. These were tentatively assigned to nitrosoaldehyde and a (C,N,O) adduct intermediate formed by deprotonation and polymerization of *aa*-NM:



Above 373 K, these intermediate species may further decompose to form isocyanate.

Formation of *aci*-anion nitromethane upon adsorption of nitromethane on a variety of oxides with basic sites has been confirmed by Lima *et al.*⁸ Using ¹³C CP/MAS NMR, they have shown that in the cases of γ -Al₂O₃, MgO, and Mg(Al)O oxides, proton abstraction by basic sites leads to formation of *aa*-NM, which is stabilized by the conjugate Lewis acid site. Moreover, they identify a direct correlation between the chemical shift of the carbon atom of adsorbed nitromethane and the heat of adsorption of CO₂ on the same material. As this heat of adsorption is proportional to the basicity of the surface sites, Lima *et al.*⁸ have shown that NM can be used as an accurate NMR probe for monitoring the basicity of oxide surfaces.

The results obtained by these groups^{6,8} indicate that upon adsorption on alumina, surface decomposition of NM can take place at relatively low temperatures, below 373 K. Moreover, specific processes such as the rearrangement reaction of NM with formation of *aci*-nitromethane (a-NM) or deprotonation reactions of a-NM can play important roles in the chemistry of NM on the aluminum oxide surface. However, the precise mechanism of these reactions and formation of a-NM and *aa*-NM compounds is not yet available.

Despite the experimental interest in understanding the catalytic properties of nitro compounds on alumina, to the best of our knowledge no theoretical studies are available to date. We note, however, some related work by Allouche.⁹ By using *ab initio* cluster calculations, he investigated the adsorption of nitromethane on MgO(100) and CaO(100) surfaces and determined the catalytic action of these basic oxides on deprotonation reactions.

In order to clarify some of the fundamental issues related to the interactions of energetic materials, particularly nitro compounds, with the Al₂O₃ surface, in the present work we focus on atomic-level descriptions of the interactions between the energetic compounds NM and 1,1-diamino-2,2-dinitroethylene (FOX-7) with the α -alumina surface. This study represents an extension of our recent density functional theory (DFT) results of the adsorption and decomposition of the same molecular systems, NM and FOX-7, on the Al(111) surface.¹⁰ In that case, we determined that oxidation of the aluminum surface readily occurs by partial or complete dissociation of the oxygen atoms from the NO₂ groups in NM and FOX-7. In the case of dissociative chemisorption, abstraction of one or both O-atoms of a nitro group by Al surface atoms was seen to be the dominant mechanism. The dissociated oxygen atoms form strong Al-O bonds with the neighboring Al sites around the dissociation sites. Additionally, the radical species obtained as a result of oxygen atom elimination remain bonded to the surface.

In the current study, we analyze similar issues related to the adsorption of NM and FOX-7 on the aluminum oxide surface. In addition, as suggested by experimental studies, particularly in strongly basic solutions, the tautomeric form of NM, *aci*-nitromethane (a-NM) can also be seen as an adsorbed species on the oxide surface.⁷ Our current study

does not try to emulate the conditions found in liquid solutions. Rather, they correspond to experiments performed under ultra high vacuum conditions. Nevertheless, we have considered in the present work not only an analysis of the chemisorption properties of NM and FOX-7 but also the adsorption and decomposition properties of a-NM.

This paper is organized as follows: in Section II we describe the computational methods used to perform the adsorption calculations. The results and corresponding discussions of the total energy calculations for adsorption and dissociation of NM and *aci*-NM tautomers are presented in Section III. In the same section we analyze the corresponding results for the FOX-7 molecule. We summarize the main conclusions in Section IV.

II. Computational Methods

The calculations performed in this study were done using the Vienna *ab initio* simulation package (VASP).¹¹⁻¹³ This program evaluates the total energy of periodically repeating geometries based on DFT 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.^{14,15} Periodic boundary conditions are used, with the one-electron pseudo-orbitals expanded over a plane-wave basis set. The expansion includes all plane waves with kinetic energy $\hbar^2 k^2 / 2m < E_{\text{cut}}$, where k is the wave vector, m the electronic mass, and E_{cut} is the cutoff energy. In this study, a cutoff energy of 495 eV is chosen that ensures convergence with respect to the basis set.

Calculations were performed using the generalized gradient approximation (GGA) DFT with the PW91 exchange-correlation functional.¹⁶ The sampling of the Brillouin zone was performed using a Monkhorst-Pack scheme.¹⁷ The minimization of the electronic free energy was performed using an efficient iterative matrix-diagonalization routine based on a sequential band-by-band residuum minimization method (RMM)^{12,13} or alternatively based on preconditioned band-by-band conjugate-gradient (CG) minimization.¹⁸ The optimization of different atomic configurations was performed by conjugate-gradient minimization of the total energy.

The minimum energy paths between distinct minima were evaluated by use of the nudged elastic band (NEB) method of Jónsson and co-workers.¹⁹ In this approach, the reaction path is “discretized,” with the discrete configurations, or images, between minima being connected by elastic springs to prevent the images from sliding to the minima in the optimization.

III. Results and Discussion

A. Test Calculations for Bulk α -Al₂O₃ and Al₂O₃(0001) Surface.

A number of tests have been initially performed to verify the accuracy of the method when applied to bulk Al₂O₃, the bare alumina surface, and to the isolated NM and FOX-7 molecules, and to clarify different technical aspects such as the optimum cutoff energy for these calculations.

The 10-atom rhombohedral primitive cell of α -Al₂O₃ has been optimized using a cutoff energy of 495 eV. In these calculations, a Monkhorst-Pack grid of 3x3x3 has been used, leading to 14 irreducible k-points in the Brillouin zone. Based on a fit of the

dependence of the unit cell energy on the corresponding cell volume with the Murnaghan equation of state,²⁰ an optimum volume of the unit cell of 86.6076 Å³ has been determined. This value is 2.2% higher than the experimental values reported by Wyckoff ($V_{0,\text{exp}}=84.7116 \text{ Å}^3$)²¹ and 1.7% higher than that of d'Amour *et al.*²² ($V_{0,\text{exp}} = 85.1087 \text{ Å}^3$). The corresponding rhombohedral unit parameters are $a_{\text{calc}} = 5.162 \text{ Å}$ and $\alpha_{\text{calc}} = 55.27^\circ$. These values are within 0.5% of the experimental values of $a_{\text{exp}} = 5.136 \text{ Å}$ and $\alpha_{\text{exp}} = 55.30^\circ$, measured by d'Amour *et al.*²² The positions of the Al- and O-ions were calculated to be $u(\text{Al}) = 0.352$ and $u(\text{O}) = 0.556$, which are essentially identical to those obtained experimentally.²¹ The bulk modulus at zero pressure and its pressure derivative obtained from a Murnaghan analysis were $B_{0,\text{calc}} = 2.31 \text{ Mbar}$ and $B'_{0,\text{calc}} = 3.92$. The corresponding values reported by d'Amour *et al.*²² were $B_{0,\text{exp}} = 2.54 \text{ Mbar}$ and $B'_{0,\text{exp}} = 4.27$. Finally, the cohesive energy of the rhombohedral unit cell per Al₂O₃ unit was determined to be 31.52 eV, which is very close to the experimental value of 31.8 eV.²³ These results indicate that the present set of pseudopotentials is able to provide a very good representation of the structural and energetic properties of bulk Al₂O₃.

The surface model employed in this study corresponds to the (0001) basal plane of α -Al₂O₃. Using the optimized unit cell values, a supercell model was constructed containing 2x2 surface units with three layers of O atoms (36 ions) and six layers of Al atoms (24 ions). The surface slab is separated by a vacuum layer of 12 Å from the neighboring slabs in the direction perpendicular to the surface. It has been shown in previous studies that an Al-terminated Al₂O₃(0001) surface is energetically the most stable.^{24,25} Consequently, we adopt the same surface termination in the present work. A 3x3x1 Monkhorst-Pack grid of k-points has been used in optimization calculations.

Initial surface optimizations have been performed by relaxing all ions in the systems. We have determined that the surface energy decreases from the 3.58 J/m² corresponding to the unrelaxed structure to 1.51 J/m² after relaxation. This significant reduction of surface energy by a factor well over 2 was also noted by Manassidis *et al.*²⁴ based on LDA calculations. Our surface energy is basically identical to that obtained by Jarvis *et al.*²⁵ of 1.5 J/m² using DFT-GGA calculations and only slightly larger than the value of 1.42 J/m² obtained based on the same computational method by Alavi *et al.*²⁶ As a result of surface optimization, significant inward relaxations of about 0.8 Å take place for the surface Al atoms, which are positioned almost in the same plane with the O atoms. The vertical separation between the top plane of Al atoms and the immediate next plane of O atoms is only 0.04 Å. For the surface top layer, the Al-O bonds decrease from the bulk value of 1.87 Å to 1.69 Å. These values are close to those reported by Jarvis *et al.*²⁵ and Alavi *et al.*²⁶

B. Test calculations for isolated NM and FOX-7 molecules

In a previous study²⁷ dedicated to analysis of the structural and electronic properties of crystalline FOX-7, we have shown that plane-wave DFT calculations using the VASP code can be used to provide an accurate description of the structural properties of this molecule as well as of the corresponding crystal structure. The details of this analysis will not be repeated here. In this section we will only focus upon results related to the gas phase nitromethane tautomers which can interact with the Al₂O₃ surface.

Isolated NM and *aci*-NM molecules have been optimized in a cubic box of 12x12x12 Å³. For nitromethane, both the staggered and eclipsed conformations (see

Figures 1a and 1b) have been considered. Similarly, for the *aci* form of nitromethane, $\text{CH}_2=\text{NO}_2\text{H}$, we have analyzed both the *cis* and *trans* configurations (see Figures 1c and 1d). The corresponding structural and energetic parameters are given in Table 1. From the analysis of the energetic data given in Table 1 it can be seen that the staggered and eclipsed conformations of NM have almost identical energies, with an extremely small difference of 0.029 kcal/mol. This result is similar to that by Lammertsma *et al.*²⁸ based on *ab initio* calculations at MP2/6-31G*, MP4/6-31G* and MP4/6-311+G** levels. They computed the energetic difference between the eclipsed and staggered configurations of NM to be 0.025 kcal/mol at the MP4/6-311+G** level, which is practically identical to the present result. Similarly, the energy difference between the staggered configuration of nitromethane and the *cis* configuration of a-NM (see Figure 1c) was computed by Lammertsma and Prasad^{28,29} to be 14.14 kcal/mol at G1 or G2³⁰ levels of theory. Our calculations predict a difference of 11.9 kcal/mol, in good agreement with the previous high level *ab initio* results. Moreover, we found that in the case of the *aci*-NM molecule, the *cis* isomer is more stable than the *trans* isomer by 5.7 kcal/mol. This difference agrees well with the Lammertsma and Prasad result²⁹ of 6.7 kcal/mol, determined at the G2 level of theory.

The differences in the geometrical parameters of the staggered and eclipsed conformations of the NM molecule, summarized in Table 1, are minimal. Additionally, there is a good agreement between the predicted and experimental values³¹ for the majority of geometric parameters. The largest deviation is seen in the N-O bond lengths, for which the computed values are about 1.3% larger than experiment. This slight overestimation is found in other *ab initio* predictions as well. For example, Lammertsma

and Prasad²⁸ have calculated practically identical N-O bond lengths, $r(\text{N-O}) = 1.24 \text{ \AA}$, at the MP2/6-31G* level to those computed in the present study.

Good agreement also has been found between our calculated geometric parameters of *cis aci*-NM and those reported by Lammertsma and Prasad.²⁸ A comparison of these two sets of values is provided in Table 1. The largest difference of $0.023 \text{ \AA}$ is seen for the case of N-O1 bond of *aci*-NM. In the case of *trans aci*-NM isomer, optimized under C_s symmetry at MP2/6-31G* level, Lammertsma and Prasad²⁸ found that this corresponds to a transition state. We have optimized the *trans aci*-NM isomer without imposing the C_s symmetry constraint. We found a local minimum corresponding to a structure where H1 atom of *aci*-NM is out of the molecular plane (see Figure 1d), with torsion angle $\tau(\text{C-N-O1-H1}) = -19.1^\circ$.

The agreement between our results for NM, FOX-7 and *cis a*-NM systems with either experimental values or other high-level *ab initio* calculations indicates that the present theoretical description of individual molecules and their isomers is adequate. Additionally, we have seen that good descriptions of both structural and energetic data for both the bulk oxide system and for the bare surface are obtained. The accuracy of these theoretical predictions lends confidence to the next step of our investigation, namely the interactions of NM and FOX-7 molecules with the $\text{Al}_2\text{O}_3(0001)$ surface.

C. Nitromethane Adsorption on $\text{Al}_2\text{O}_3(0001)$ Surface.

C1. Geometries and Energies.

The adsorption studies of NM on the $\alpha\text{-Al}_2\text{O}_3(0001)$ surface were done using the 2×2 supercell described above. Adsorptions at several surface sites and for distinct

orientations of the NM molecule relative to the surface were first examined. The adsorption energies calculated throughout this work were obtained based on the expression

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

where E_{molec} is the energy of the isolated adsorbate molecule in its equilibrium position, E_{slab} is the total energy of the 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. The energy of the isolated adsorbate molecule was determined from calculations performed on a single molecule in a cubic cell with sides of 12 Å. The same Brillouin-zone sampling has been used to calculate the energies of the bare slab and of the molecule-slab systems.

The first set of adsorption configurations we investigated corresponds to the case in which the NM molecule is adsorbed with the C-N bond perpendicular to the surface and the nitro group oriented towards the surface. Several initial positions of the molecule on the surface were considered, of which three representative configurations are depicted in Figure 2. Panels a1-c1 in Figure 2 show the initial starting configuration while panels a2-c2 show the final, optimized configurations. For clarity and ease of notation, these final configurations will be denoted as NM(I), NM(II), NM(III), respectively. In the optimization process, all the atoms of the slab model and of the NM molecule were allowed to relax, with the exception of the bottom Al and O layers of the slab. In panels a1-c1 of Figure 2, we illustrate the cases in which the NM molecule was placed initially on top of O and Al atoms of the surface or above a fcc hollow site. As indicated in panels

a2-c2 of Figure 2, independent of the initial configuration of the NM molecule, adsorption on the surface takes place by initial bonding of one of the oxygen atoms of the nitro group to an Al atom of the surface. The geometric parameters of the NM molecule adsorbed on the surface for each of the three optimized configurations depicted in Figure 2 are given in Table 2 together with the corresponding calculated binding energies. For all of these vertical configurations, the binding energies have similar values in the range 19.3-19.7 kcal/mol. The lengths of the Al-O bonds formed upon adsorption range between 1.939-1.942 Å. Relative to the isolated molecule, the N-O1 bond involved in bonding to the surface is stretched by about 0.34-0.38 Å while the other N-O2 bond is slightly compressed by 0.02 Å. The existence of a strong interaction between NM and the oxide surface is also reflected by an upward shift of 0.63-0.71 Å of the Al atom involved in bonding relative to the initial relaxed surface structure.

We have also investigated the case where the NM molecule was initially oriented perpendicular to the surface but with the methyl group directed toward the surface (not shown). We have analyzed two cases: one in which the C-N bond was positioned above an Al atom and the other one above an O atom from the top layer. For both these two configurations, we have determined only very weak adsorption minima with binding energies between 0.97–1.13 kcal/mol. Consequently, NM adsorption with the methyl group directed toward the surface is not favorable and has not been pursued further in this study.

Another set of optimizations has been done in which the initial configuration of the NM molecule has both the C-N bond and the NO₂ group parallel to the surface. Several cases were tested in which the initial position of the N atom was placed either above an Al

or O atom of the surface or above the hollow sites. The final results are similar and we present a representative case, denoted hereafter as NM(IV), in Figure 3. As indicated in this figure, during the optimization process the nitro group, initially parallel to the surface (see Figure 3a), rotates to minimize the repulsive interactions with O atoms of the surface. In the final configuration (see Figures 3b and 3c), the nitro group is practically perpendicular to the surface plane, leading to an eclipsed conformation of the NM molecule. In this configuration, the major binding of the molecule to the surface takes place through the Al1-O1 bond. Additionally, as illustrated in Figure 3c where a top view of the adsorption configuration of NM(IV) structure is shown, two of the H atoms of the methyl group are directly pointing to the surface O atoms (see, for example, the atoms H3 and surface Os1 atom in Figure 3c), indicating a weak attractive interaction. Using notation from Figure 3c, the corresponding H...O distances are: $r(\text{H3-Os1}) = 2.126 \text{ \AA}$, $r(\text{H2-Os2}) = 2.399 \text{ \AA}$, $r(\text{H2-Os3}) = 2.752 \text{ \AA}$. In this parallel adsorption configuration, the binding energy of the NM molecule increases to 26 kcal/mol. This value is about 7 kcal/mol higher than the one determined for the vertical adsorption configuration indicating a more stable adsorption configuration. This energetic increase is also reflected in the modifications of the molecular geometric parameters given in Table 2. Relative to the vertical configurations, the most significant change in the parallel configuration is in the Al1-O1 bond, which decreases from about 1.94 Å in NM(I,II,III) to 1.906 Å in NM(IV). The corresponding N-O1 bond is stretched to 1.284 Å and slight elongations of C-H bonds to 1.097-1.104 Å are present due to the attractive interactions of the H atoms with the surface oxygen atoms.

As illustrated in Figure 3c, the C-N bond of NM(IV) structure is essentially oriented along the Al1...Al2 direction. We have tested also the case where the C-N bond is aligned along Al1...Os1 direction as presented in Figure 3d). In this case, for the final optimized structure, NM(V), none of the H atoms of the methyl group are pointing directly towards O atoms of the surface. The closest H...O distances are $r(\text{H3-Os1}) = 2.487 \text{ \AA}$ and $r(\text{H2-Os1}) = 2.566 \text{ \AA}$. The binding energy of this structure, 25.3 kcal/mol, is slightly smaller than that for NM(IV).

C2. Electrostatic Charges.

A common tool for obtaining a semi-quantitative measure of charge transfer is the Mulliken population analysis³² in which the electronic charge is partitioned among the individual atoms. This partitioning has been done in the present study using the periodic boundary condition version of the DFT program DMOL³ developed by Delley.^{33,34} DMOL³ uses a basis set of numeric atomic functions that are exact solutions to the Kohn-Sham equations for the atoms. In this study, calculations have been done using a double numeric polarized (DNP) basis set and the nonlocal Perdew-Wang (PW91) functional within generalized-gradient approximation.³⁵ The Mulliken charges for the isolated NM molecule in both the staggered and eclipsed configurations and for the vertical (NM (II)) and parallel (NM(IV)) adsorption configurations are summarized in Table 3. As expected, the largest changes in atomic charges are found for the O atoms of the nitro group. The negative charge of the O atom involved in Al-O bonding decreases from -0.31e for the isolated NM molecule to -0.39e for NM(II) and -0.40e for NM(IV), respectively. The charge of the other O atom of the nitro group has a reverse variation. Specifically, its

charge becomes less negative, ranging from -0.31e in the gas phase to -0.19e for NM(II) and -0.2e for NM(IV). Concomitantly, the positive charge of the Al atom involved in bonding increases slightly from 1.11e for the isolated slab to 1.28e for NM(II) and 1.30e for NM(IV). The interaction of NM with the surface also leads to a net increase of the positive charge of H atoms. Specifically, from values around 0.12e corresponding to the isolated molecule, the H-atom charge increases to 0.16-0.17e in the vertical upward configuration and to about 0.2 e for the H atoms closest to the surface for the parallel adsorption configuration. These changes reflect the fact that the major interaction with the surface takes place through one of the O atoms of the nitro group, with a small contribution due to polarization of the H atoms of the methyl group.

The above changes can be put into better perspective if we compare them with those observed in the interactions of NM with the Al(111) surface.¹⁰ In that study, it was shown that even in the case of nondissociative adsorption, there is a significant increase in the negative charge of the O atoms in NM of about -0.3e relative to gas phase. A similar decrease of about 0.4e was found to take place in the positive charge of the N atom. Naturally, with this transfer of electrons to the NM molecule, there is a corresponding increase in the positive charge of the Al atoms bonded to the NM molecule, with values in the range 0.38-0.51e. It can be concluded that in the case of the oxide surface, the transfer of charge is smaller than in the case of the metallic surface. This observation is also consistent with the lack of dissociative chemisorption of the NM molecule adsorbed on the oxide surface, in contradistinction to the case of metallic Al surface.

C3. Minimum Energy Potential Path for Adsorbate Interconversion.

As described in the previous section, adsorption of nitromethane can take place through two main configurations: (a) a vertical orientation in which bonding takes place between the O atom of the nitro group and an Al atom of the surface, and (b) a parallel configuration where contributions to surface bonding are provided by both the O atom of the nitro group and some of the H atoms of the methyl group. In this section, computations of the reaction pathway and energy necessary for interconversion among these two adsorbate configurations are described. Such calculations have been done using the NEB method where the initial and final states correspond to the vertical and parallel adsorption configurations, respectively. The results of these calculations are depicted in Figure 4. As seen in this figure, the potential energy surface in the region of upright configuration is very shallow. There is a small activation energy of about 1.8 kcal/mol for the interconversion from the upright to the parallel configuration. These results indicate that the upright configuration is only a metastable minimum on the potential energy surface. Upon initial bonding of the nitromethane to one of the Al surface atoms, rotation around the corresponding N-O bond (for the O atom involved in direct bonding to Al) can easily take place, leading to the more stable parallel configuration.

C4. Minimum Energy Path for NM Dissociation.

Starting from the parallel adsorption configuration of NM on $\text{Al}_2\text{O}_3(0001)$ surface (NM(IV)), we have analyzed two minimum energy pathways for molecular dissociation. The first corresponds to CH bond scission with formation of a surface OH bond. The

second pathway corresponds to the C-N bond dissociation with formation of adsorbed CH_3 and NO_2 species. In both cases, the calculations of the minimum energy pathways were done using the NEB method for seven images distributed along the reaction pathway. The results are presented in Figures 5a and 5b. The initial and final adsorption configurations are depicted below the individual potential curves in Fig. 5. The geometric parameters of the CH_2NO_2 radical obtained by H elimination, denoted henceforth as RNM1, are provided in Table 2. In this case, the radical adsorbs through an Al-O bond with a length of 1.755 Å while the newly formed hydroxyl group has a bond of 0.977 Å. The separation $\text{H1}\cdots\text{C}$ between the H atom of the newly formed hydroxyl group and the C atom from where dissociation took place is quite large, with a value of 3.237 Å. The total charge of the RNM1 radical evaluated using the Mulliken charges given in Table 3 is -0.57e.

As can be seen from the plot 5a, the activation energy for the CH bond rupture reaction is about 13.8 kcal/mol. The other process, corresponding to C-N bond breaking, has a higher activation energy of about 37 kcal/mol. The activation energies of both reactions are significantly smaller than the corresponding energies for these reactions in the gas phase. For example, the C-H bond dissociation energy of gas phase nitromethane was estimated to be 88.1 kcal/mol³⁶ while for the C-N bond strength a value of 58.5 kcal/mol has been reported.³⁷ By comparing these values with our calculated NEB barriers, it follows that the Al_2O_3 surface significantly decreases the CH and CN bond dissociation energies in NM.

D. *Aci*-Nitromethane Adsorption on Al₂O₃(0001) Surface.

D1. Geometries and Energies.

As was indicated in the Introduction, the formation of *aci*-nitromethane (a-NM) species on aluminum oxide surfaces has been inferred in several previous experimental studies, particularly on γ -alumina.^{6,8} In this study we have investigated the adsorption properties of both the *cis* and *trans* a-NM species on α -Al₂O₃(0001). Here the *cis* and *trans* forms differ in the orientation of the OH group relative to the NO bonds. For the adsorbed a-NM molecule, either the O atom which is bonded to the Al surface atom or the O atom pointing away from the surface can carry the hydroxyl group. Furthermore, each of these two isomers can exist in *cis* and *trans* forms, for a total of four possible configurations. Pictorial views of these configurations are given in Figure 6 while selected geometric parameters together with the corresponding binding energies are given in Table 2.

When the OH group is on the side of the a-NM molecule toward the surface (configuration a-NM(I) in Figure 6a), the binding energy of 24.2 kcal/mol is slightly smaller than for NM(IV) (26.0 kcal/mol). This energy is evaluated with respect to the energies of the isolated slab and the isolated *cis* isomer of a-NM. However, when the binding energy is calculated with respect to the total energy of the isolated slab and of the isolated gas phase NM molecule, the corresponding value is only 12.3 kcal/mol. For the adsorbed a-NM, the molecular plane is perpendicular to the surface and contains the Al1-Os surface atoms. Such a configuration maximizes the attractive interactions between the O1...Al1, O1H1...Os and C-H2...Os2 pairs of atoms. At equilibrium the O1-Al1 bond

length is about 1.884 Å while the distance from the H1 and H2 atoms to the closest O atoms of the surface are 2.822 and 2.209 Å, respectively. As in the case of parallel NM adsorption, the Al atom bonded to a-NM is displaced above the surface by about 0.54 Å.

In addition to the *cis* a-NM(I) configuration, we have also obtained the optimized *trans* a-NM configuration, in which the OH group is on the side of the molecule facing the surface. The final configuration a-NM(II) is represented in Figure 6b. In this case the O1H1 bond is rotated outward relative to the C-N-O1 plane with a torsional angle $\tau(\text{C-N-O1-H1}) = -100.04^\circ$. The total binding energy of this configuration is 1.8 kcal/mol smaller than that for the a-NM(I) structure. The most significant structural changes for the *cis* a-NM(I) and *trans* a-NM(II) configurations, relative to the corresponding geometries of the isolated *cis* and *trans* a-NM species, are the lengthening of the N-OH bonds, which reach values of 1.63 Å and 1.73 Å, respectively, indicating a significant weakening of this bond upon absorption on the surface. Note that subsequent analysis of the potential energy surface (presented in section D3) has indicated that this configuration is not a local minimum but rather a transition state.

Finally, the other two configurations we have analyzed correspond to *cis* and *trans* forms for the case when the OH bond is on the side of the nitro group pointing away from the surface. These configurations, denoted as a-NM(III) and a-NM(IV), are illustrated in Figures 6c and 6d. In these cases the binding energies relative to the isolated NM molecule and the isolated surface are 19.7 kcal/mol and 13.7 kcal/mol for *cis* and *trans*, respectively. Therefore, among the four a-NM configurations, the a-NM(III) state corresponding to a *cis* tautomer with the OH group away from the surface is the most stable, followed by the *trans* a-NM(IV) tautomer. The increase in the binding energies of

a-NM(III) and a-NM(IV) species is reflected also by a corresponding decrease of the Al1-O2 bond lengths to about 1.866 Å for both *cis* and *trans* tautomers. Similarly, the close contacts H2...Os2 decrease to 1.987 Å for a-NM(III) and 1.933 Å for a-NM(IV), respectively, while the lengths of the C-H bonds pointing toward the surface increase to 1.098 and 1.101 Å, respectively. Referring now to the intramolecular geometric parameters, the differences in the *cis* a-NM(III) and *trans* a-NM(IV) configurations include a lengthening of the N-OH bond from 1.391 Å in the former to 1.403 Å in the latter. Likewise, the length of the C-N bond increases from 1.286 Å to 1.291 Å. Such geometric variations have also been noted for the isolated gas phase systems and have been associated with a repulsive electrostatic interaction between the *aci*-nitro hydrogen and the methylene group existent in the *trans* state.²⁸

D2. Electrostatic Charges.

Based on DMOL³ calculations as described in section C2, we have calculated the Mulliken charges for the four a-NM tautomeric species. The results are listed in Table 3, including those obtained for the isolated molecules. By comparing the two sets of values, we notice that, as in the case of the NM molecule, the largest charge variations occur on the O- and H- in the hydroxyl group. For the isolated *cis* and *trans* systems, the net charges on the hydroxyl group O- and H-atoms (O1+H1 atoms in Table 3) are -0.105e and -0.065e, respectively. The corresponding values for adsorbed *cis* species are -0.176e for a-NM(I) and -0.194 for a-NM(III), while for the *trans* species they are -0.205e for a-NM(II) and -0.162e for a-NM(IV), respectively. More pronounced charge variations are seen for the H atom of the CH₂ group pointing to the surface (H2 atoms in Table 3)

and for the Al atom involved in bonding to the molecule. The positive charge on the H atom increases by about 0.11e while for the Al atom the increase is in the range 0.169-0.202e. Overall, the total charge transferred from a-NM(III) (0.162e) and a-NM(IV) (0.166e) to the surface is slightly larger than the charge transfer observed for a-NM(I) (0.112e) and a-NM(II) (0.13e), which is consistent with the larger binding energies for the two former tautomer configurations.

D3. Minimum Energy Potential Path for NM $\leftrightarrow$ *aci*-NM Tautomerism and Dissociation of a-NM(I).

In this section we investigate the energetic requirements for the tautomeric reaction NM $\leftrightarrow$ *aci*-NM taking place on the Al₂O₃ (0001) surface. As previously discussed, several distinct adsorption configurations of *aci*-NM are found in which the OH group can be located either on the side of a-NM toward the surface or towards the vacuum side. In particular, we have considered two reaction pathways. The first one corresponds to the rearrangement reaction NM(IV) $\rightarrow$ a-NM(III) $\rightarrow$ a-NM(IV) while the second reaction corresponds to NM(IV) $\rightarrow$ a-NM(II) $\rightarrow$ a-NM(I).

The results of NEB calculations for the process NM(IV) $\rightarrow$ a-NM(III) $\rightarrow$ a-NM(IV) are illustrated in Figure 7a. Molecular structures corresponding to selected points along the reaction pathway in Figure 7a are also represented at the bottom of this figure. Figure 7b shows the corresponding energy profile for the reaction in the gas phase. From Figure 7b it is seen that the gas phase tautomerization reaction NM $\rightarrow$ *trans* a-NM has an energy barrier of about 59 kcal/mol. From the *trans* a-NM configuration (see image 8 in Figure 7b) the OH bond can further rotate to reach the *cis* a-NM (image 14 in

Figure 7b) configuration with a very small activation energy of less than 0.2 kcal/mol. When the tautomerization reaction $\text{NM(IV)} \rightarrow \text{a-NM(III)}$ takes place on the Al_2O_3 (0001) surface, the results of our NEB calculations shown in Figure 7a indicate a decrease of the activation energy by about 8 kcal/mol to about 51 kcal/mol. As illustrated in Figure 7a, once the system reaches the *trans* a-NM(IV) state (image 9 in Figure 7a), the corresponding barrier to form *cis* a-NM (III) (image 17 in Figure 7a) is extremely small with a value of about 0.1 kcal/mol. From these calculations it follows that if energy in excess of 51 kcal/mol is available, formation of *cis* a-NM(III) tautomer is possible.

We have also analyzed the potential energy surface for the tautomerization reaction $\text{NM(IV)} \rightarrow \text{a-NM(II)} \rightarrow \text{a-NM(I)}$. Based on this analysis (not shown), we have found an activation energy of 56 kcal/mol, slightly larger than the one determined for $\text{NM(IV)} \rightarrow \text{a-NM(IV)} \rightarrow \text{a-NM(III)}$. Additionally, the analysis of the potential surface around the NM(II) configuration indicates that this corresponds to a transition state rather than a local minimum.

Figure 8 shows the minimum energy pathways for the H-atom transfer reactions between the O atoms of the *cis* a-NM tautomers. As in the previous case, Figure 8a illustrates the case in which the reaction takes place on the surface ($\text{a-NM(III)} \rightarrow \text{a-NM(I)}$) while Figure 8b corresponds to the case when reaction occurs in the gas phase. The atomic configurations depicted at the bottom of the figure correspond to the image numbers given in Figure 8a. As expected, the gas phase reaction profile in Figure 8b is symmetric and the calculated activation energy is about 23 kcal/mol for H-atom migration between the O atoms of the nitro group. For the corresponding reaction on the surface (Figure 8a), the activation energy in the forward direction, $\text{a-NM(III)} \rightarrow \text{a-NM(I)}$, is not

changed significantly ($E_b \sim 23.9$ kcal/mol.) However, the reverse process has a smaller activation energy of only 15.2 kcal/mol.

Beside tautomerization reactions of NM, we have also analyzed an H-atom dissociation reaction of a-NM(**I**), for which the potential energy pathway is shown in Figure 9. In this process, the H1 atom of a-NM(**I**) migrates from the molecule to the surface, thereby breaking the O1-H1 bond and forming a new OH bond on the surface (denoted as Os-H1.) The resulting CH_2NO_2 radical also remains adsorbed on the surface. The geometric parameters of this radical, denoted henceforth as RNM2, are given in Table 2. The newly formed hydroxyl group has a bond length $r(\text{Os-H1}) = 0.984 \text{ \AA}$ while the separation between H1 and the oxygen O1 of the CH_2NO_2 radical is $r(\text{O1} \cdots \text{H1}) = 2.544 \text{ \AA}$. The RNM2 radical adsorbs with an Al1-O1 bond of $1.744 \text{ \AA}$, slightly smaller than the one for the RNM1 radical obtained as a result of H dissociation from the NM molecule. Also, the total Mulliken charge of the RNM2 radical (see Table 3) is $-0.54e$, similar to the one obtained for RNM1 radical.

A summary of the calculated results for the adsorption, decomposition and tautomerization reactions of NM on the $\text{Al}_2\text{O}_3(0001)$ surface is given in Figure 10. Panel (a) shows the relative energies of the gas phase and adsorbed configurations of NM. The adsorption process takes place via initial formation of the vertical configuration NM(**II**) followed by molecular reorientation leading to the parallel adsorption configuration, NM(**IV**). Panel (b) shows the relative energies of the configurations obtained by H-atom elimination, with subsequent formation of an adsorbed RNM1 radical and a surface hydroxyl group, or by C-N bond dissociation with formation of adsorbed CH_3 and NO_2 , from the adsorbed NM(**IV**) species. The total energy of the RNM1(a)+H(a) configuration,

as well as the activation energy necessary to reach this state (evaluated in section C4) starting from adsorbed nitromethane, are smaller than those for the C-N dissociation pathway, indicating that the former process is both kinetically and thermodynamically more favorable than the latter. Finally, in panel (c) we present two sets of results. The first is a comparison of the relative energies of the *cis* and *trans aci*-NM species with respect to gas phase NM (in staggered configuration). In the gas phase *cis* a-NM(g) and *trans* a-NM(g) are less stable than NM(g) by 11.8 kcal/mol and 17.6 kcal/mol, respectively. For the adsorbed tautomeric a-NM species, two sets of results are obtained. When the OH group of *aci*-NM is far from the surface; i.e., the a-NM(III) and a-NM(IV) configurations, the relative energies of these two species with respect to adsorbed nitromethane (NM(IV)) decrease to 6.3 kcal/mol and 12.2 kcal/mol. Therefore, the surface provides an additional stabilization of about 5.4-5.5 kcal/mol of the two tautomeric forms. However, when the OH group is close to the surface as in the case of the *cis* a-NM(I) configuration, the relative energy with respect to that of adsorbed NM increases to 13.6 kcal/mol. This corresponds to an increase in tautomerization energy relative to the gas phase. Finally, the energy RNM2(a)+H(a) of the radical obtained from *aci*-NM(I) dissociation and of the adsorbed hydroxyl group is about 8.2 kcal/mol above the reference energy of adsorbed NM. This is slightly higher than the energy of RNM1+H(a) system of 6.6 kcal/mol.

E. FOX-7 Adsorption on Al₂O₃(0001) Surface.

We have shown in previous sections that interactions of NM with the Al₂O₃ surface take place primarily through the nitro group, with formation of an Al-O bond. It is

expected that similar mechanisms will also be found for other molecules containing the nitro chemical group. We have tested this in the present study for the case of 1,1-diamino-2,2-dinitroethylene (FOX-7) molecule. The main interest for this compound is due to its applications as a high energy density material with superior shock-sensitivity properties.³⁸ In our previous study¹⁰ of the interactions of nitro-containing molecules with an Al surface, we found very similar behavior for the NM and FOX-7 molecules. Particularly, we have found a common propensity for oxidation of the aluminum surface by these molecules through dissociation of the nitro groups and formation of strong Al-O bonds. Moreover, for NM and FOX-7 we found that both molecular and dissociative adsorption can take place with significant charge redistributions. In the present case, we also expect to observe similar adsorption mechanisms for NM and FOX-7 molecules on the Al₂O₃ surface.

As in the case of NM, the first sets of calculations focused on adsorption of the FOX-7 molecule starting from configurations in which the CC bond axis in FOX-7 is initially perpendicular to the surface. Figure 11 presents two such adsorption configurations. Panel a1 of Figure 11 shows an initial configuration of FOX-7 in which the C=C bond of FOX-7 is perpendicular to the surface and one of the O atoms from each nitro group is pointing towards the surface. The O atoms are positioned approximately above one Al atom in the first layer and another Al atom in the second layer of the surface, as indicated by dotted lines in Figure 11, panel a1. Panel b1 of Figure 11 illustrates another initial configuration in which the C=C bond in FOX-7 is oriented at an angle of about 55° from the surface normal and only one nitro group of the molecule points towards the surface, with one of the O atoms positioned above a surface Al atom.

The optimized configurations corresponding to adsorption on the surface starting from the initial structures given in panels a1 and b1 of Figure 11 are shown in panels a2 and b2 and are denoted as FX(I) and FX(II), respectively. In both instances, adsorption takes place molecularly with formation of new Al-O bonds between one of the O atoms of the nitro group and an Al atom beneath it, with corresponding bond lengths of 1.912-1.920 Å. Internal rotation of the molecules to minimize the repulsive interaction between O atoms of the nitro groups and O atoms of the surface also takes place. The computed adsorption energies for the two configurations are 19.7 kcal/mol and 22.8 kcal/mol, respectively. These values are very close to those obtained for the vertical configurations of nitromethane, namely NM(I), NM(II) and NM(III), with values in the range 19.1-19.8 kcal/mol. As a result of adsorption, significant upward dislocation of the Al atoms involved in molecular bonding occurs, with displacements of 0.6 Å for FX(I) and 0.63 Å for FX(II), respectively.

A second set of configurations in which the FOX-7 molecules is initially oriented parallel to the surfaces also has been investigated. Figure 12 shows three representative parallel adsorption configurations, denoted as FX(III), FX(IV) and FX(V), respectively.

Panels a and b of Figure 12 are lateral and top views of a configuration (FX(III)) in which the FOX-7 molecule is adsorbed parallel to the surface such that bonding to surface Al atoms takes place between one of the N atoms of an amine group (denoted as N1) and one of O atoms of a nitro group (denoted as O2). Due to repulsive electrostatic interactions with surface O atoms, the other nitro group is rotated away from the surface towards the vacuum. In this configuration, the N1-Al1 and O2-Al2 bond distances are $r(\text{N1-Al1}) = 2.10 \text{ Å}$ and $r(\text{O2-Al2}) = 1.945 \text{ Å}$, respectively. In the amine group in which

the N atom is bonded to the surface Al atom, there is also an upward pyramidalization of the H atoms. In the other amine group, one H atom (denoted as H1 in Figure 12a) is tilted towards the surface, indicating a hydrogen bond to one of the surface oxygen atoms (indicated with a yellow circle in Figure 12b). The corresponding distance $r(\text{H1}\cdots\text{O})$ is 2.131 Å. As a result of the multiple bonds between the FOX-7 molecule and surface, (i.e., the Al-NH₂ and Al-NO₂ bonds as well as the N-H $\cdots$ O-Al hydrogen bond,) the adsorption energy is 35.6 kcal/mol, significantly larger than for the vertical adsorption configuration.

In the FX(IV) configuration depicted in panels c and d of Figure 12, the molecular orientation on the surface is such that simultaneous bonding of both nitro groups to the Al surface atoms can take place. One O atom from each nitro group is bonded to an Al surface atom while the other O atom of each nitro group is rotated away from the surface, due to repulsive electrostatic interactions with the surface O atoms. The corresponding Al-O bond distances are $r(\text{Al1-O1}) = 1.931$ Å and $r(\text{Al2-O2}) = 1.942$ Å. For this configuration, both nitro groups participate in surface bonding as do both amino groups. Specifically, each amino group has one of its hydrogen atoms involved in hydrogen bonding to the O surface atoms. These O atoms are marked in Figure 12d with yellow circles. The corresponding NH $\cdots$ O hydrogen bonds are 2.49 Å and 1.857 Å. The total adsorption energy for this configuration is 45.9 kcal/mol.

Finally, panels e and f in Figure 12 show an adsorption configuration in which three of the four H atoms in FOX-7 participate in hydrogen bonds to the surface O atoms, in addition to formation of an Al-O bond from each of the nitro groups. The hydrogen atoms are denoted as H1, H2, and H3 and the corresponding surface O atoms are

identified by yellow circles. The corresponding NH-O bond distances are: $r(\text{H1}\cdots\text{O}) = 2.162 \text{ \AA}$, $r(\text{H2}\cdots\text{O}) = 2.317 \text{ \AA}$, $r(\text{H3}\cdots\text{O}) = 2.138 \text{ \AA}$, respectively, while the length of the remaining $\text{H}\cdots\text{O}$ pair is $2.791 \text{ \AA}$, larger than the usual range of hydrogen bonds. The Al-O bond lengths are $r(\text{Al1-O1}) = 1.934 \text{ \AA}$ and $r(\text{Al2-O2}) = 1.909 \text{ \AA}$, which are similar to the corresponding bond distances in FOX-7(III,IV). The binding energy is the highest of the five configurations of FOX-7 adsorbed on $\text{Al}_2\text{O}_3(0001)$ surface, with a value of 48.4 kcal/mol .

The results presented in this section indicate, as in the case of the NM system, the most stable adsorption configurations of the FOX-7 molecule are parallel to the surface. In these cases, multiple bonding can take place. We have identified states in which both nitro and amino groups can be involved in bonding to the surface. The primary bonding takes place through formation of Al-O or Al-N bonds. Additionally, the H atoms of FOX-7 can form hydrogen bonds to surface O atoms. It should also be noted that FOX-7 also contains intramolecular hydrogen bonds, $\text{NH}\cdots\text{ON}$. For example, in the case of the FOX(V) structure, the intramolecular hydrogen bond distances have values of $2.341 \text{ \AA}$ and $1.896 \text{ \AA}$, with $\text{O2}\cdots\text{H4}$ with the shorter bond length (See Figure 12f). Due to the size of the FOX-7 molecule, we have not attempted to determine the activation energies for various bond dissociation channels of this molecule adsorbed on the surface. However, due to the strong interaction with the surface, it is expected that bond dissociation energies will be smaller than those present in the gas phase. This subject will remain open for future study.

IV. Conclusions

The interactions of the NM and FOX-7 molecules with the $\text{Al}_2\text{O}_3(0001)$ surface have been investigated based on optimizations performed using plane-wave density functional theory calculations with the PW91 exchange-correlation functional.

The first objective of this study was to determine the adsorption mechanisms for these molecular species on the oxide surface. Particularly, our calculations indicate that initial binding takes place through formation of Al-O bonds to the nitro group of NM or one of the nitro groups of FOX-7. The corresponding binding energies for such vertical configurations are similar, with values in the range 19.1-19.8 kcal/mol for NM and 19.7-22.8 kcal/mol for FOX-7. However, for both these molecular species the most stable adsorption configurations result when the molecules lay parallel to the surface. For such geometries, the binding energies increase to 26 kcal/mol for NM and 35.6-48.4 for FOX-7. The larger adsorption energies of the FOX-7 molecule are due to the existence of multiple Al-ONO or Al-NH₂ bonds as well as to formation of one or more NH $\cdots$ O hydrogen bonds with surface oxygen atoms.

The second objective of this work was to identify possible decomposition pathways of NM on the oxide surface and to evaluate the corresponding activation energies. We have determined that as a result of adsorption on the surface there are significant variations in the bond dissociation energies of NM relative to the gas phase. Our calculations have indicated that H scission reactions can take place with a small activation energy of about 14 kcal/mol, while in the case of the C-N bond dissociation reaction leading to adsorbed CH₃ and NO₂ fragments, the activation energy is about 38 kcal/mol. Both values are significantly smaller than the corresponding activation

energies in the gas phase.

The next objective of this study was to investigate the adsorption properties of various tautomeric forms of NM. In particular, we have analyzed four *aci*-NM tautomers and have determined that, relative to the isolated NM molecule and isolated slab surface, the corresponding adsorption energies are 12.3, 10.5, 19.6 and 13.7 kcal/mol for *aci*-NM(**I**), *aci*-NM(**II**), *aci*-NM(**III**) and *aci*-NM(**IV**), respectively. The minimum energy reaction pathways for H migration from NM(**IV**) with formation of *cis aci*-NM species, or for H migration among different types of *aci*-NM species having *cis* configurations, have also been investigated. We found that the reaction NM(**IV**)→a-NM(**III**) has a barrier of about 51 kcal/mol, about 9 kcal/mol smaller than that in the gas phase. In contrast, the H migration reaction *aci*-NM(**III**) → *aci*-NM(**I**) has been found to have an activation energy of about 24.8 kcal/mol, similar to that in the gas phase. However, the reverse reaction *aci*-NM(**I**) → *aci*-NM(**III**) has a smaller activation energy of 17 kcal/mol. The nonequivalent behavior of the two *cis aci*-NM(**I**) and *aci*-NM(**III**) configurations is also reflected by the difference in their binding energies, with the latter energetically preferred by about 8 kcal/mol. Finally, in the case of the a-NM(**I**) tautomer, we have also investigated the minimum energy pathway for C-H bond dissociation with subsequent formation of a surface OH group. This process has a barrier slightly larger than the one found for direct H-atom elimination from NM, with a value of about 19 kcal/mol. Our calculations also indicate that additional stabilization is provided by the oxide surface for the tautomeric forms a-NM(**III**) and a-NM(**IV**) in which the OH group is far from the surface. Indeed, the relative energies between the *cis* and *trans* a-NM tautomers and NM decrease by about

5.5 kcal/mol relative to the gas phase when tautomerization takes place on the surface. However, this additional stabilization has not been observed in the case of a-NM(**I**) tautomer in which the OH group is close to the surface.

Our final objective was to determine if other nitro-containing molecules such as FOX-7 exhibit similar adsorption characteristics as NM. We found, in analogy with the results for NM, a propensity of FOX-7 to adsorb on the surface via formation of Al-O bonds and an energetic preference for formation of parallel, rather than vertical, configurations. However, the parallel conformations of FOX-7 on the aluminum oxide surface also exhibited the ability to form Al-N bonds as well as one or more hydrogen bonds between the amine hydrogen atoms of FOX-7 and surface O atoms.

The validity of the present set of results is restricted to the case of a perfect oxide surface without defective sites. As this is clearly an approximation of the aluminum oxide surface, further investigations to address the influence of the surface defective sites upon the chemisorption and reaction properties of nitro-containing molecules should also be considered in future.

Acknowledgements

The authors gratefully acknowledge grants of computer time at the Army Research Laboratory, Aeronautical System Center, the Engineer Research and Development Center, and the Naval Oceanographic Office Major Shared Resource Centers, sponsored by the Department of Defense High Performance Computing Modernization Program. DLT gratefully acknowledges support by the U.S. Army Research Office under grant number DAAD19-01-1-0503.

References

1. Sutton, G. P., “*Rocket Propulsion Elements*”, John Wiley & Sons, Inc., 1992.
2. Politzer, P.; Lane, P.; Grice, M. E. J. *Phys. Chem. A* **2001**, 105, 7473.
3. Price, E. W. *Prog. Astronaut. Aeornaut.* **1984**, 6, 479.
4. Kwok, Q. S. M.; Fouchard, R. C.; Turcotte, A.M.; Lightfoot, P.D.; Bowes, R. *Propellants, Explosives, Pyrotechnics* **2002**, 27, 229.
5. Ivanov, G. V.; Tepper, F. in “*Challenges in Propellants and Combustion 100 Years After Nobel*”, K. K. Kuo (Eds), Begell House, New York 1997, p.636.
6. Yanaguchi, M. J. Chem. Soc., Faraday Trans., **1997**, 93, 3581.
7. Nesternko, N.; Lima, E.; Graffin, P.; Charles de Ménorval, L.; Laspéras, M.; Tichit, D.; Fajula, F. *New J. Chem.* **1999**, 23, 665.
8. Lima, E.; Charles de Ménorval, L.; Tichit, D.; Laspéras, M.; Graffin, P.; Fajula, F. *J. Phys. Chem. B* **2003**, 107, 4070.
9. Allouche, A. *J. Phys. Chem.* **1996**, 100, 1820
10. D. C. Sorescu, J. A Boatz, D. L. Thompson, *J. Phys. Chem. B* **2003**, 107, 8953.
11. Kresse, G.; Hafner, J. *Phys. Rev.* **1993**, B 48, 13115.
12. Kresse, G.; Furthmüller, J. *Comput. Mat. Sci.* **1996**, 6, 15.
13. Kresse, G.; Furthmüller, J. *Phys. Rev.* **1996**, B 54, 11169.
14. Vanderbilt, D. *Phys. Rev.* **1990**, B 41, 7892.
15. Kresse, G; Hafner, J. *J. Phys. Condens. Matter* **1994**, 6, 824.
16. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pedersen, M. R.; Singh, D. J.; Frolhais, C. *Phys. Rev.* **1992**, B 46, 6671.
17. Monkhorst, H. J.; Pack, J. D. *Phys. Rev.* **1976**, B 13, 5188.

18. Kresse, G; Hafner, J. *Phys. Rev.* **1993**, B 47, 588.
19. Jónsson, H.; Mills, G. Jacobsen, K. W. *Nudged elastic band method for finding minimum energy paths of transitions.* In *Classical Quantum Dynamics in Condensed Phase Simulations*; Berne, B. J., Ciccotti, G., Coker, D. F., Eds.; World Scientific: Singapore. 1998; p 385.
20. Murnaghan, F. D. *Proc. Natl. Acad. Sci USA* **1944**, 30, 2344.
21. Wyckoff, W. R. G, *Crystal Structures*, 2nd ed., Interscience, New York, 1964, vol. 2.
22. d'Amour, H.; Schiferl, D.; Denner, W.; Schulz, H.; Holzapfel, W. B. *J. Appl Phys.* **1978**, 49, 4411.
23. *CRC Handbook of Chemistry and Physics*, 67th ed.; CRC: Boca Raton, FL., 1983.
24. Manassidis, I.; De Vita, A.; Gillan, M. J. *Surf. Sci. Lett.* **1993**, 285, L517.
25. Jarvis, E. A. A.; Carter, E. A. *J. Phys. Chem. B* **2001**, 105, 4045.
26. Alavi, S.; Sorescu, D. C; Thompson, D. L. *J. Phys. Chem. B* **2003**, 107, 186.
27. Sorescu, D. C.; Boatz, J. A.; Thompson, D. L. *J. Phys. Chem. A* **2001**, 105, 5010.
28. Lammertsma, K.; Prasad, B. V. *J. Am. Chem. Soc.* **1993**, 115, 2348.
29. Lammertsma, K.; Prasad, B. V. *J. Am. Chem. Soc.* **1994**, 116, 642.
30. Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, 90, 5622.
31. Jeffrey, G. A.; Ruble, J. R.; Wingert, L. M.; Yates, J. H.; McMullan, R. K. *J. Am. Chem. Soc.* 1985, 107, 6227.
32. Mulliken, R. S. *J. Chem. Phys.* **1955**, 23, 1833, 2343.
33. Delley, B. *J. Chem. Phys.* **1990**, 92, 508.

34. Delley, B. *J. Chem. Phys.* **2002**, 113, 7756.
35. Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, B45, 13244.
36. McKee, M. L. *J. Am. Chem. Soc.* **1986**, 108, 5784.
37. Batt, L.; Robinson, G. N. *The Chemistry of Amino, Nitroso, and Nitro Compounds and their Derivatives*; Patai, S., Ed. Wiley: New York, 1982.
38. Latypov, N. V.; Bergman, J.; Langlet, A.; Wellmar, U.; Bemm, U. *Tetrahedron* **1998**, 54, 11525

Table. 1 Comparison of the calculated geometric parameters for nitromethane and *aci*-nitromethane to the previously reported experimental^{b)} and theoretical^{c)} values.

Parameter ^{c)}	NM staggered	NM eclipsed	NM exp. ^{a)}	<i>aci</i> -NM <i>cis</i>	<i>aci</i> -NM <i>cis</i> , theor. ^{b)}	<i>aci</i> -NM <i>trans</i>
r(C-N)	1.498	1.497	1.489	1.302	1.313	1.309
r(N-O ₁)	1.241	1.240	1.224	1.448	1.425	1.467
r(N-O ₂)	1.241	1.240	1.224	1.248	1.236	1.232
r(C-H ₁)	1.094	1.089	1.088	...	...	...
r(C-H ₂)	1.090	1.093	1.088	1.080	1.077	1.081
r(C-H ₃)	1.090	1.093	1.088	1.080	1.076	1.081
r(O-H ₁)	...	...	...	0.983	0.981	0.981
Θ(O ₁ NO ₂)	125.6	125.6	125.3	115.4	115.8	112.6
Θ(CNO ₁)	117.2	117.8	117.3	113.6	...	117.1
Θ(CNO ₂)	117.2	116.6	117.3	131.0	131.2	130.2
Θ(NCH ₁)	106.6	108.7	107.5	...	...	...
Θ(NCH ₂)	108.3	107.1	107.5	118.3	116.3	120.2
Θ(NCH ₃)	108.3	107.1	107.5	116.8	118.1	116.7
Θ(NOH ₁)	...	...	...	99.7	99.5	105.7
ΔE	0.0	0.029		11.857		17.654

^{a)}Microwave experimental data from Jeffrey *et al.*, Ref. 31. ^{b)}MP2/6-311+G* results from Lammertsma and Prasad, Ref. 28. ^{c)}Bond distances are given in Angstroms, bond angles in degrees, total energies in eV, and relative energies ΔE in kcal/mol.

Table. 2 Representative bond geometries and adsorption energies for nitromethane (NM), aci-nitromethane (a-NM) and dissociated radicals (RNM) adsorbed on Al₂O₃(0001) surface.

Parameter ^{a)}	NM(I)	NM(II)	NM(III)	NM(IV)	NM(V)	a-NM (I)- <i>cis</i>	a-NM (II)- <i>tr</i>	a-NM (III)- <i>cis</i>	a-NM (IV)- <i>tr</i>	RNM1	RNM2
r(C-N)	1.481	1.484	1.484	1.478	1.477	1.288	1.284	1.286	1.291	1.316	1.312
r(N-O ₁)	1.277	1.274	1.278	1.284	1.280	1.628	1.728	1.391	1.403	1.401	1.421
r(N-O ₂)	1.217	1.218	1.217	1.219	1.219	1.219	1.207	1.303	1.287	1.247	1.245
r(C-H ₁)	1.097	1.095	1.095	1.088	1.089	...	...	...	...	...	...
r(C-H ₂)	1.089	1.089	1.089	1.104	1.098	1.090	1.085	1.098	1.101	1.081	1.083
r(C-H ₃)	1.091	1.091	1.092	1.097	1.097	1.085	1.087	1.083	1.084	1.082	1.082
r(O ₁ -H ₁)	...	...	...			0.980	0.980	0.985	0.981	0.977	0.984
r(Al ₁ -O ₁)	1.938	1.938	1.942	1.906	1.915	1.884	1.875	1.866	1.866	1.749	1.744
E _{ads} (1) ^{b)}	19.8	19.6	19.1	26.0	25.3	24.2	22.4	31.5	31.1		
E _{ads} (2)						12.3	10.5	19.6	13.7		

^{a)}Bond distances are given in Angstroms and binding energies in kcal/mol. The indices I-V for nitromethane correspond to the following structures: (I)- Fig.2, panel a2; (II) – Fig. 2, panel b2; (III) – Fig. 2, panel c2; (IV) – Fig. 3, panels b) and c); (V) – Fig. 3, panel d). The indices I-IV for aci-nitromethane correspond to the structures a)-d) represented in Fig. 6, respectively. RNM1 and RNM2 represent the radicals obtained by H dissociation directly from NM (see Fig. 5a, image8) or from a-NM(I) (see Fig.9, image 8).

^{b)}E_{ads}(1) (E_{ads}(2)) represents the binding energy with respect to the isolated slab and the corresponding isolated molecule (the isolated nitromethane molecule).

Table 3. Variation of Mulliken charges for nitromethane and aci-nitromethane species in gas phase and adsorbed on the Al₂O₃(0001) surface. Atomic labels are those indicated in Figure 1.^{a)}

System	C	N	O1	O2	H1	H2	H3	Al	Os1	Os2	Os3
NM(gas,stag.)	-0.083	0.329	-0.306	-0.306	0.125	0.120	0.120				
NM(gas,eclips)	-0.082	0.329	-0.308	-0.304	0.118	0.124	0.124				
a-NM(gas, <i>cis</i>)	-0.087	0.324	-0.389	-0.350	0.284	0.109	0.109				
a-NM(gas, <i>trans</i>)	-0.120	0.325	-0.333	-0.341	0.268	0.111	0.090				
aa-NM(gas)	-0.203	0.355	-0.569	-0.569		-0.007	-0.007				
Slab								1.109	-0.894	-0.894	-0.895
NM(II)	-0.151	0.362	-0.390	-0.190	0.171	0.162	0.170	1.280	-0.929	-0.929	-0.926
NM(IV)	-0.246	0.338	-0.403	-0.197	0.169	0.208	0.204	1.297	-0.948	-0.924	-0.934
RNM1	-0.232	0.361	-0.572	-0.372	0.327	0.140	0.107	1.357	-0.983	-1.000	-0.916
a-NM(I)	-0.122	0.287	-0.503	-0.253	0.327	0.221	0.155	1.311	-0.926	-0.933	-0.937
a-NM(II)	-0.109	0.249	-0.525	-0.184	0.320	0.224	0.155	1.319	-0.955	-0.926	-0.933
a-NM(III)	-0.105	0.356	-0.512	-0.286	0.318	0.238	0.153	1.286	-0.936	-0.926	-0.940
a-NM(IV)	-0.136	0.347	-0.453	-0.262	0.292	0.243	0.135	1.278	-0.938	-0.926	-0.942
RNM2	-0.228	0.344	-0.578	-0.355	0.361	0.153	0.123	1.317	-0.829	-0.946	-0.948

a) In case of NM adsorbed species, H2, H3 and O1 atoms are pointing to the surface. In the case of aci-NM species H1 denotes the hydrogen atom bonded to O atom of nitro group and H2 and O1 atoms are pointing to the surface. The labels Os1, Os2 and Os3 denote the three surface oxygen atoms bonded to the Al1 surface atom where molecular bonding takes place.

FIGURE CAPTIONS

Figure 1. Structural configurations of staggered (a) and eclipsed (b) nitromethane and of the *cis* (c) and *trans* (d) *aci*-nitromethane molecules.

Figure 2. Adsorption configurations of NM on the Al_2O_3 (0001) surface obtained from initial vertical configurations: (a) N above an O atom (NM(I)); (b) N above an Al atom (NM(II)); (c) N above a hollow site (NM(III)). The initial configurations are depicted in panels a1-c1 while the corresponding optimized configurations are presented in panels a2-c2, respectively.

Figure 3. (a-c) Adsorption configuration of NM on the Al_2O_3 (0001) surface obtained from an initial parallel configuration with NO_2 group taken parallel to the surface. The initial configuration is depicted in panel a) while the corresponding final configuration is presented in panels b) (lateral view) and c) (top view). The direction of the C-N bond is parallel to the $\text{Al1}\cdots\text{Al2}$ direction. Panel d) depicts another possible adsorption configuration of NM, where the C-N bond is parallel to the $\text{Al1}\cdots\text{Os1}$ direction. In all these figures, the O and Al atoms are colored in red and pink, respectively. For clarity, the O atoms in the second layer are shown in green.

Figure 4. Minimum energy path for interconversion of the vertical NM(III) configuration to the parallel NM(IV) adsorption configuration. The indicated images correspond to the initial, first transition state and final product configurations.

Figure 5. Minimum energy pathways for dissociation of the NM molecule starting from a parallel adsorbed configuration. Panel (a) corresponds to H scission from the methyl group with formation of adsorbed CH_2NO_2 and OH species. Panel (b) corresponds to C-N bond dissociation with formation of adsorbed CH_3 and NO_2 systems. The depicted atomic configurations correspond to the initial and final configurations of each reaction path.

Figure 6. Adsorption configurations of *cis* and *trans aci*-nitromethane on the Al_2O_3 (0001) surface. The panels a) to d) correspond to structures a-NM(I) to a-NM(IV) (see text), respectively.

Figure 7. (a) Minimum energy reaction pathway for tautomerization reaction $\text{NM(IV)} \rightarrow \text{a-NM(III)}$ on the Al_2O_3 (0001) surface. The atomic configurations indicated at the bottom of the figure correspond to a-NM(III) (image 0), first transition state (image 5), a-NM(IV) (image 9) and a-NM(III) (image 17). Figure (b) represents the minimum reaction pathway for $\text{NM} \rightarrow \text{trans a-NM} \rightarrow \text{cis a-NM}$ reactions in the gas phase.

Figure 8. (a) Minimum energy reaction pathway for migration reaction of H between the a-NM(III) and a-NM(I) structures. The geometries of the initial configuration, the transition state, and the final configuration are depicted at the bottom of the figure. Panel (b) shows the energy profile for the same reaction in the gas phase.

Figure 9. Minimum energy reaction pathway for dissociation reaction of a-NM(**I**) leading to adsorbed OH. The geometries corresponding to the initial, transition states and final states are represented at the bottom of the figure.

Figure 10. Relative energies for various configurations of adsorbed NM, *aci*-NM and radical species on Al₂O₃(0001) surface. Panel (a) refers to NM adsorption. Panel (b) corresponds to the states obtained by direct dissociation of NM. Panel (c) presents two sets of data. The first corresponds to the relative energies of *cis* and *trans aci*-nitromethane in gas phase with respect to gas phase nitromethane. The second set indicate the relative energies of *cis* and *trans aci*-NM species adsorbed on the surface together with the energy of RNM2 radical obtained by H dissociation from a-NM(**I**).

Figure 11. Adsorption configurations FX(**I**) and FX(**II**) of FOX-7 on the Al₂O₃(0001) surface obtained from initial vertical configurations: (a) The C=C bond is perpendicular to the surface and one of the O atoms from each nitro groups of the molecule are pointing towards the surface. (b) The C=C bond is oriented at about 55° from the surface normal and only one nitro group of the molecule points towards the surface. The initial configurations are depicted in panels a1) and b1) while the final optimized configurations are presented in panels a2) and b2), respectively.

Figure 12. Lateral and top views of the parallel adsorption configurations of the FOX-7 molecule. Panels (a), (b); (c), (d); and (e), (f) correspond, respectively, to FX(**III**), FX(**IV**), and FX(**V**) configurations as described in the text.

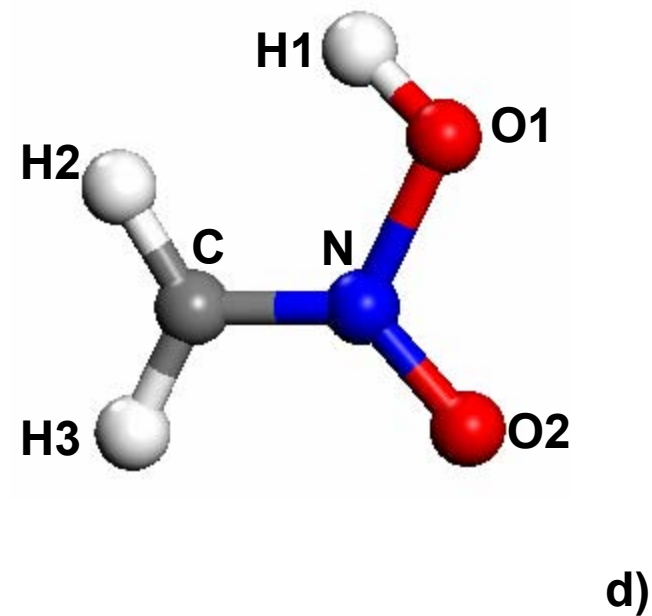
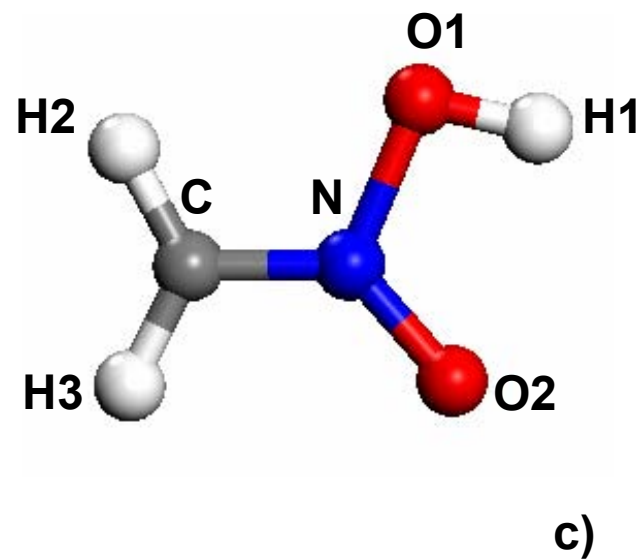
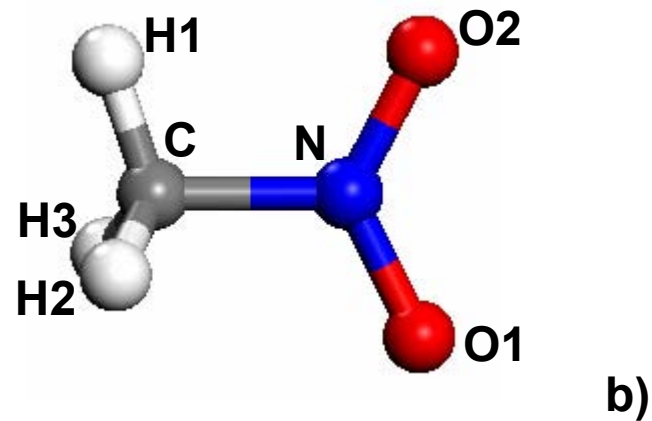
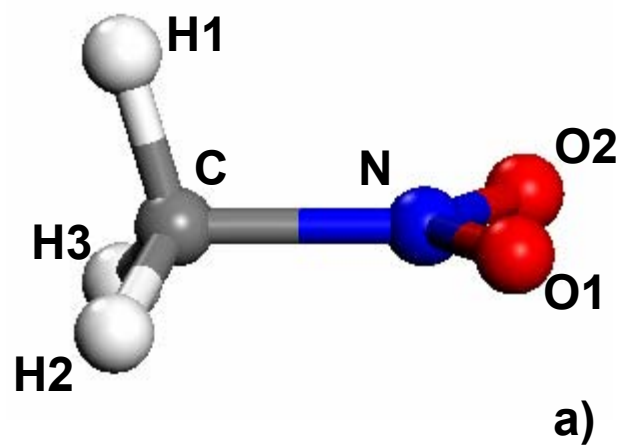


Fig. 1

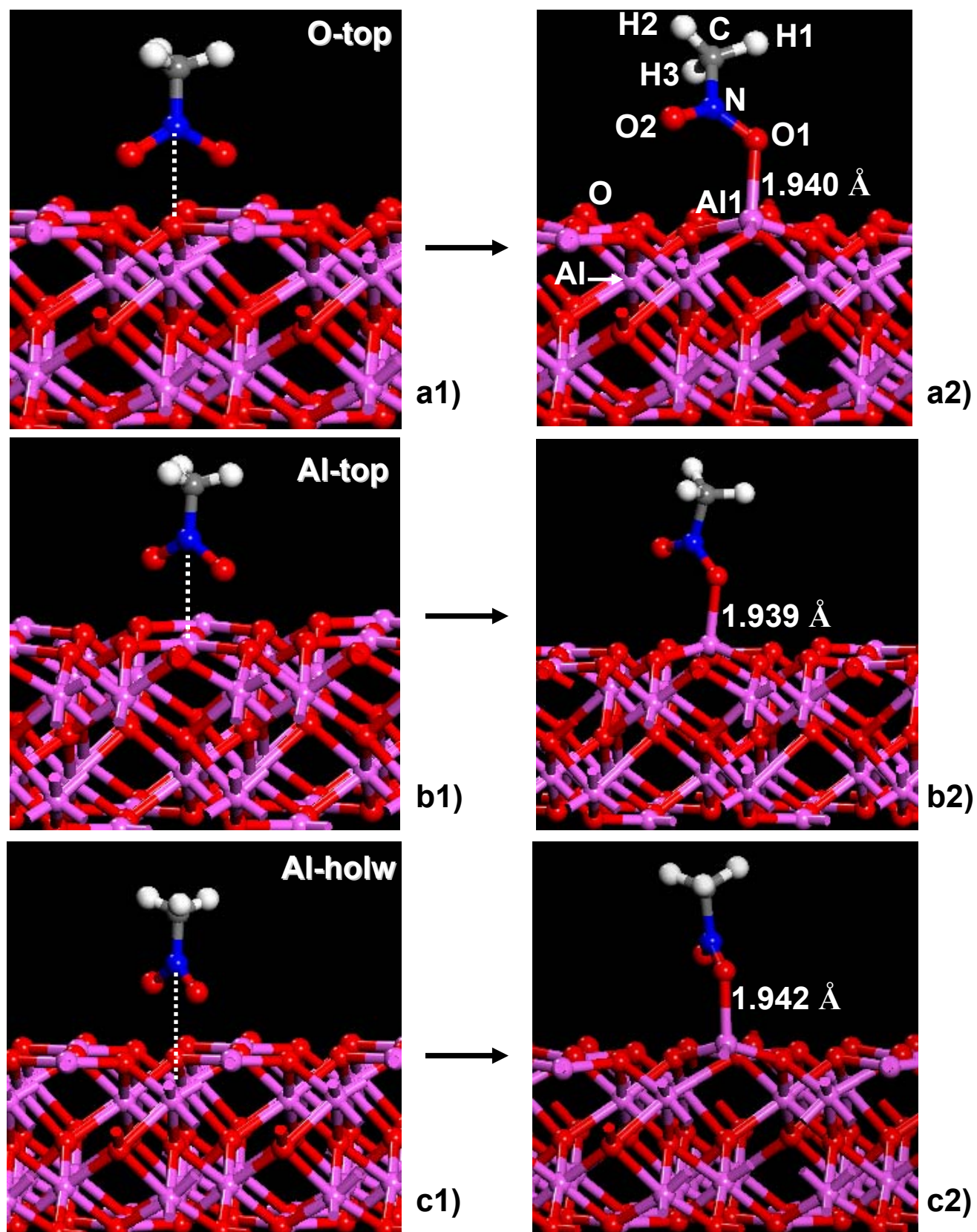
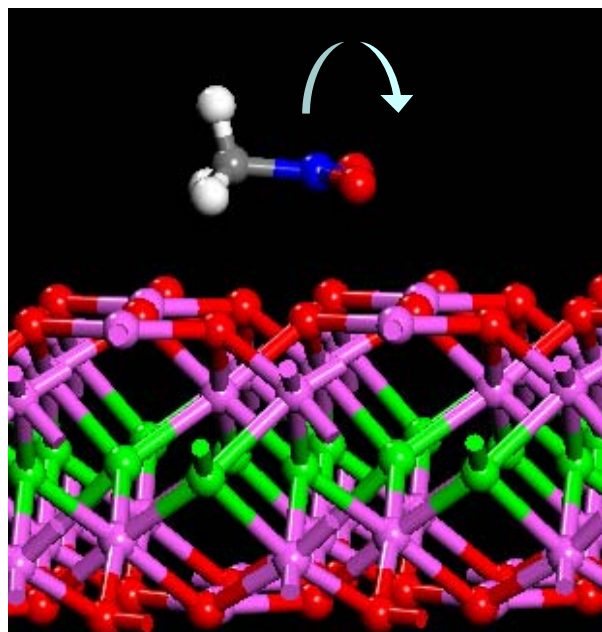
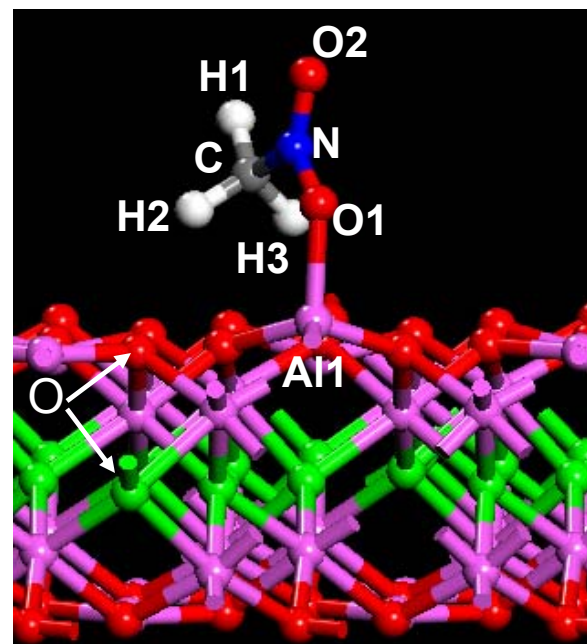


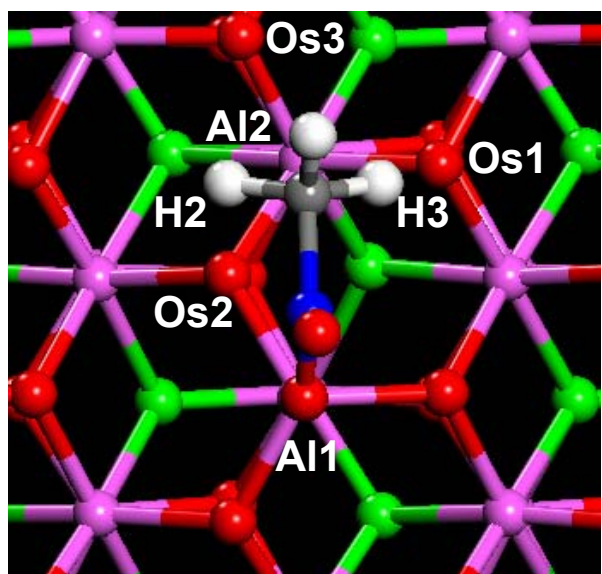
Fig. 2



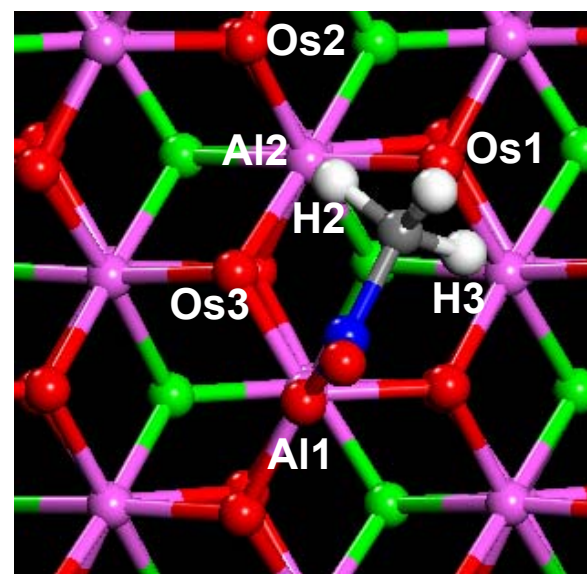
a)



b)



c)



d)

Fig. 3

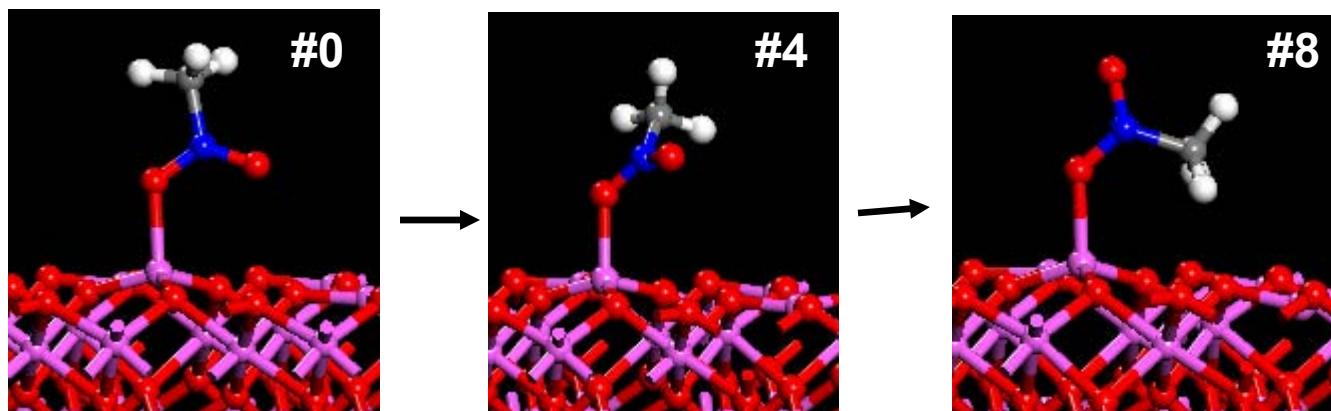
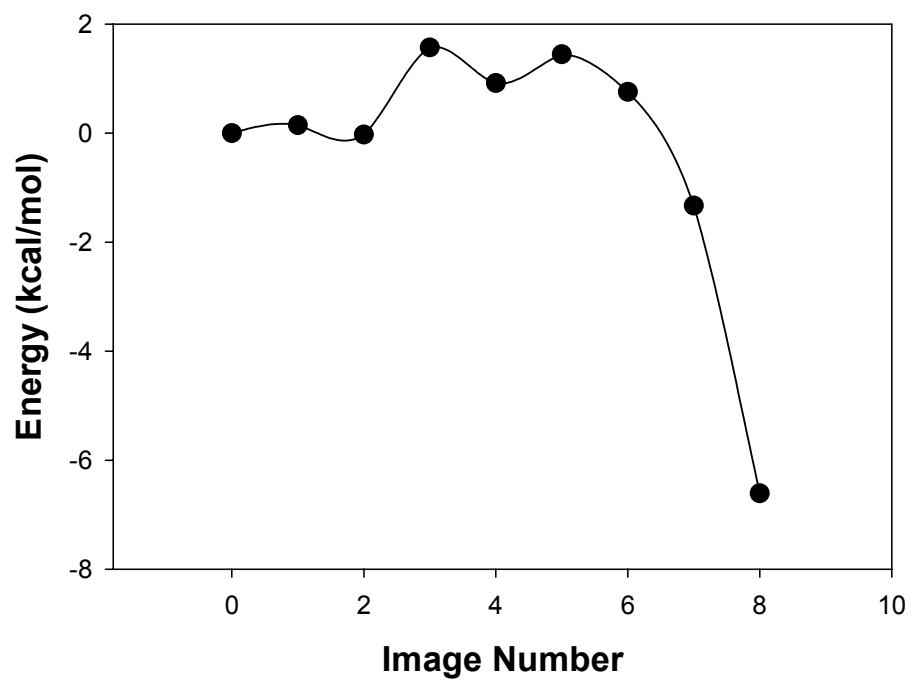


Fig. 4

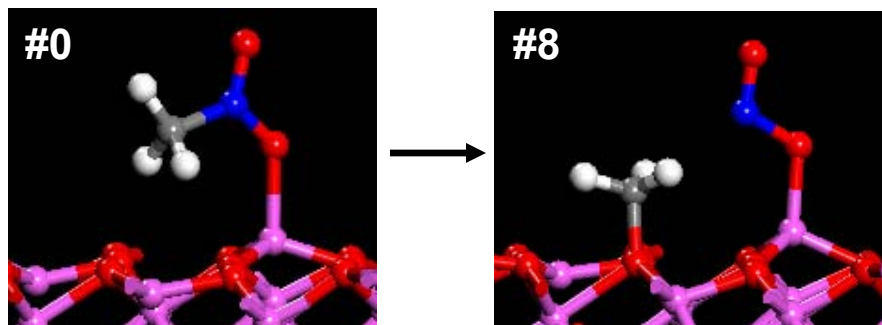
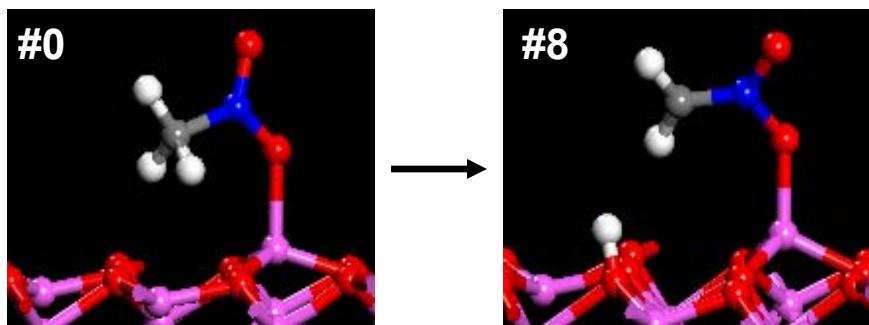
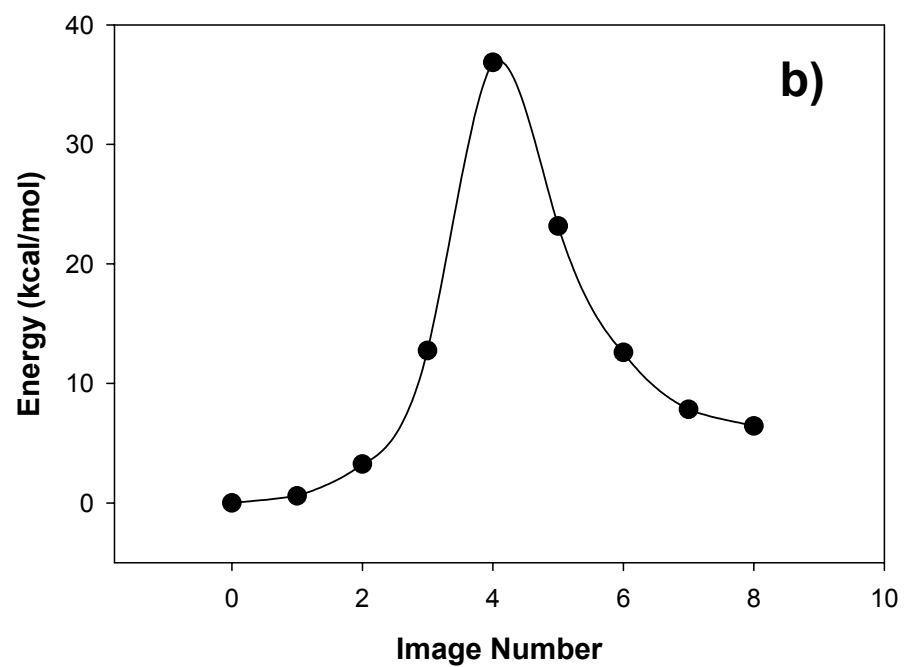
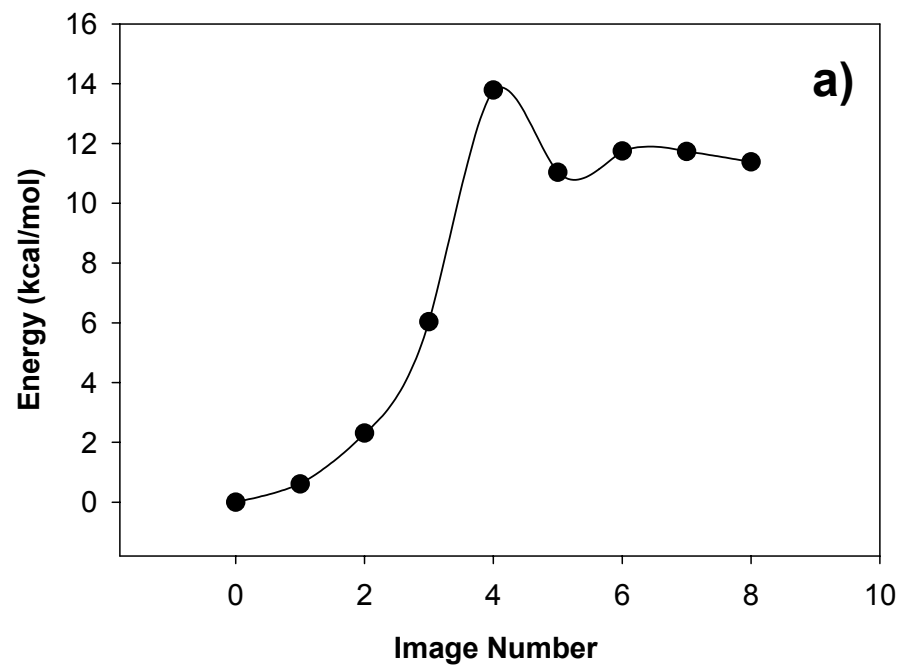
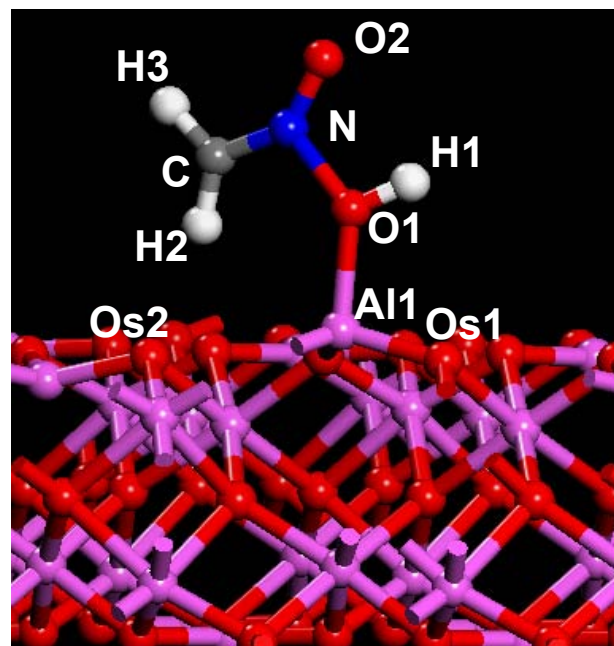
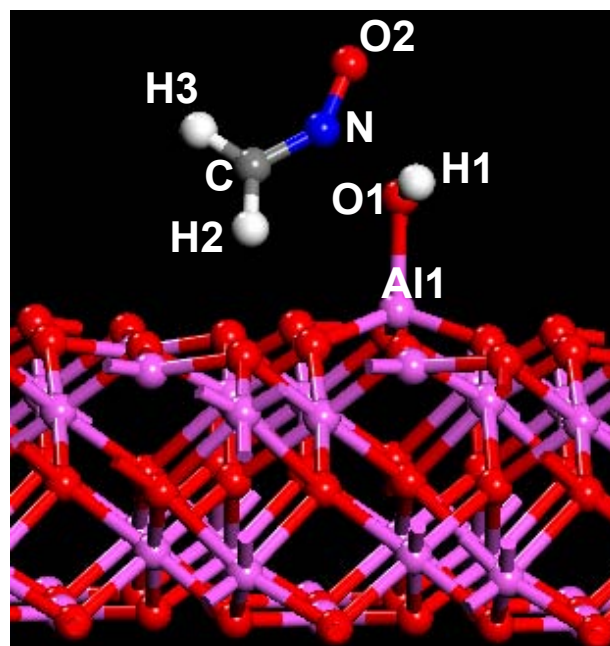


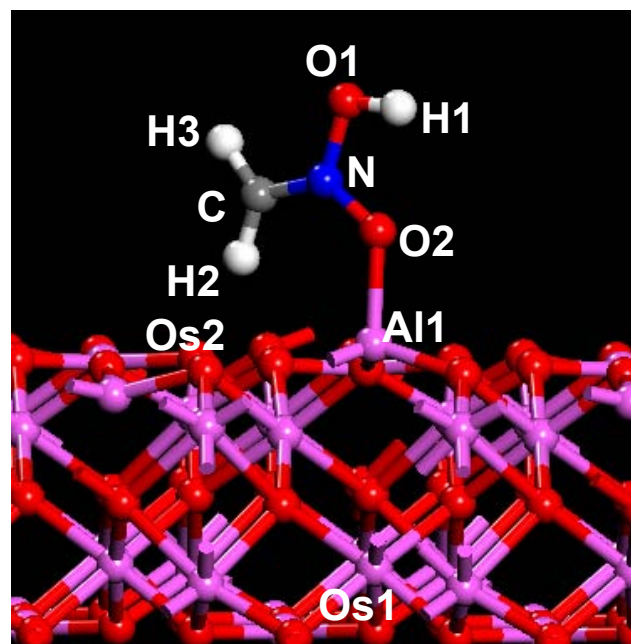
Fig. 5



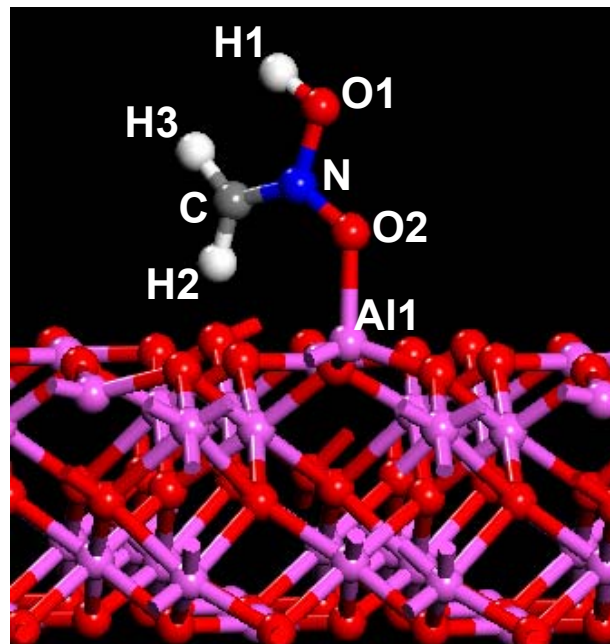
a)



b)



c)



d)

Fig. 6

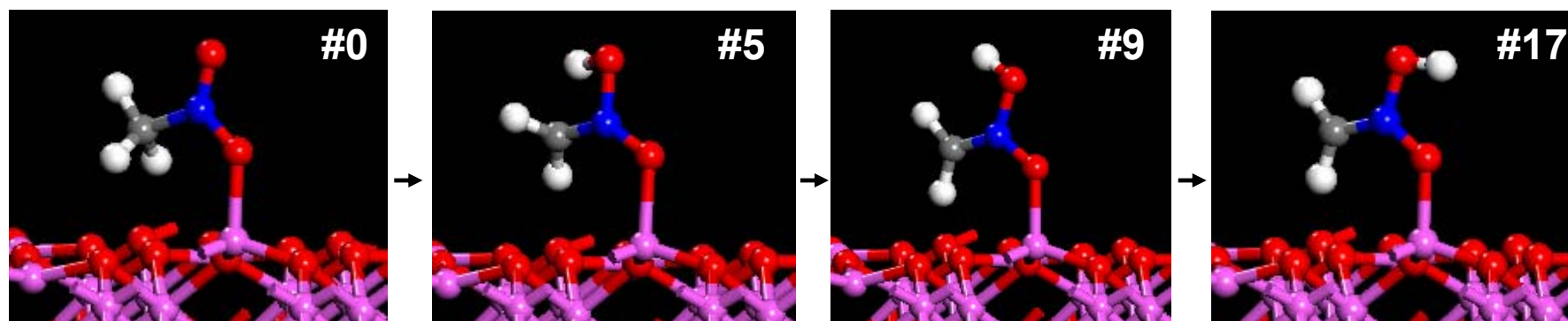
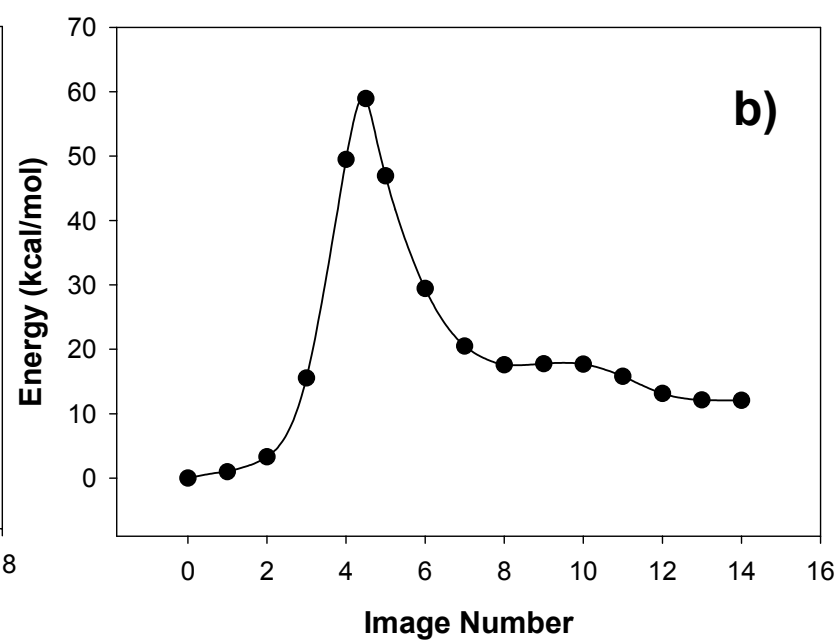
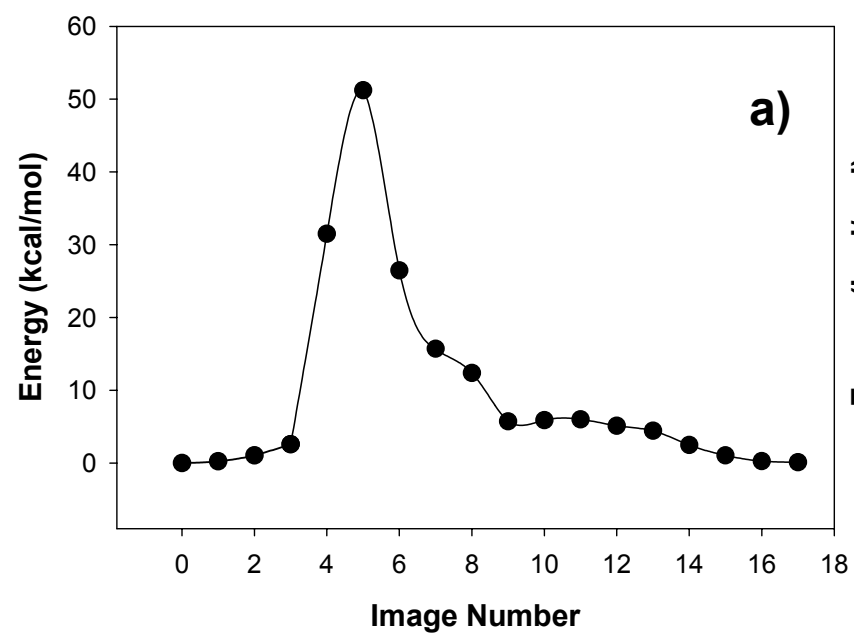


Fig. 7

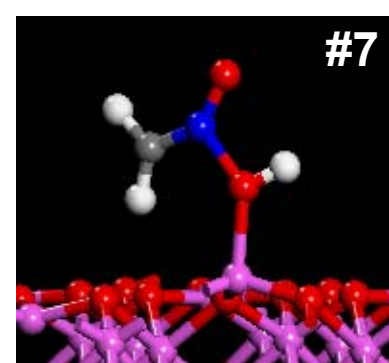
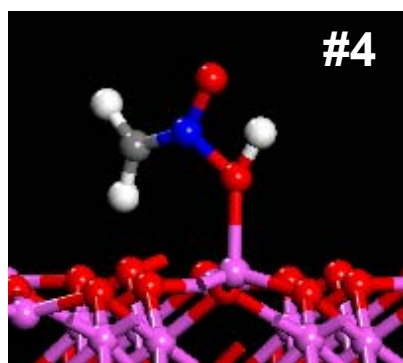
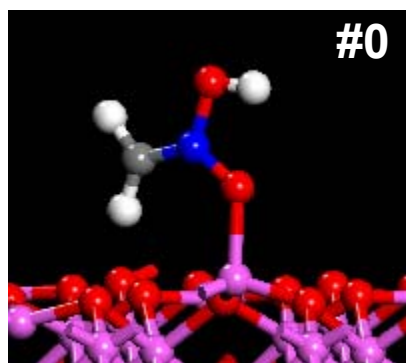
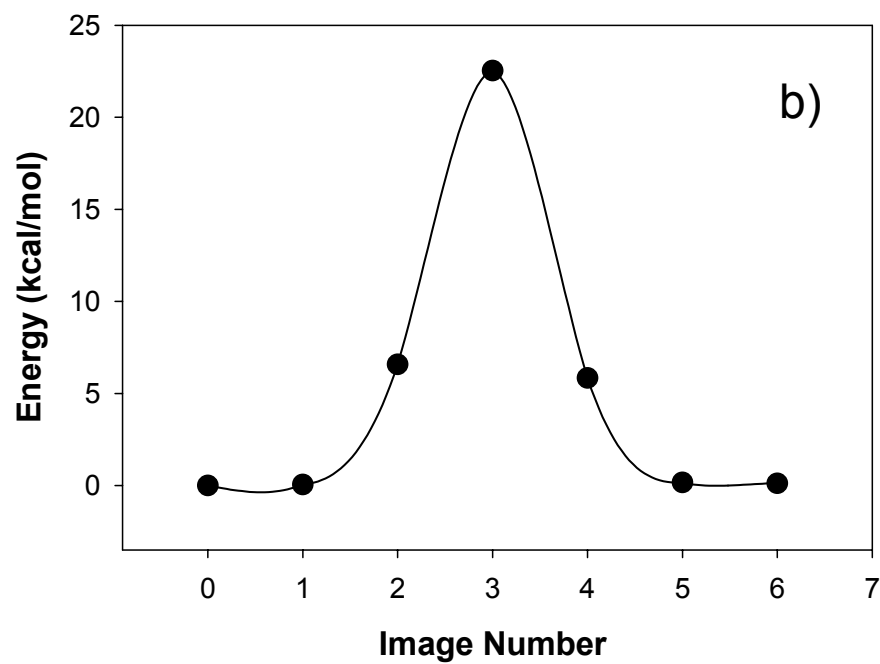
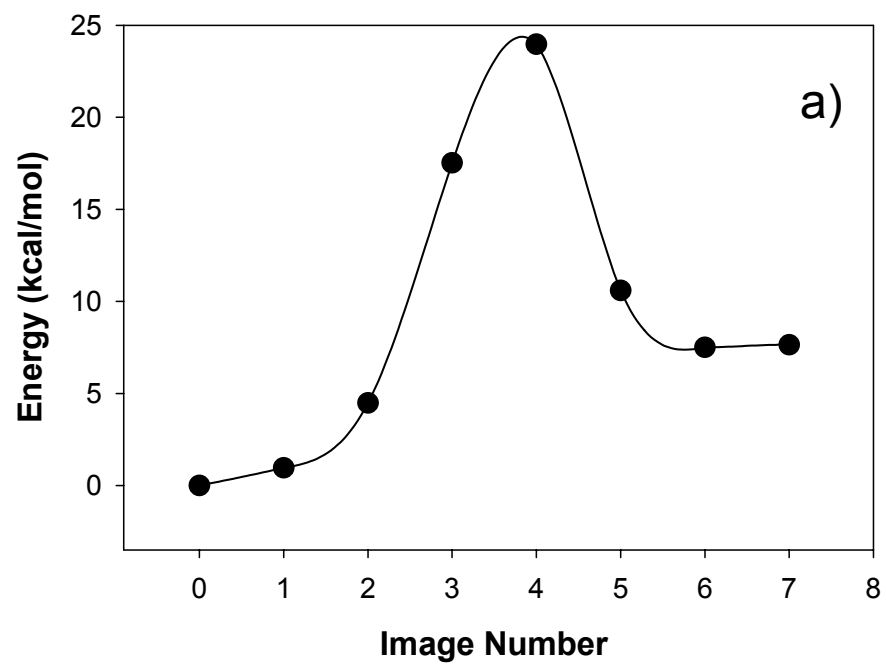


Fig. 8

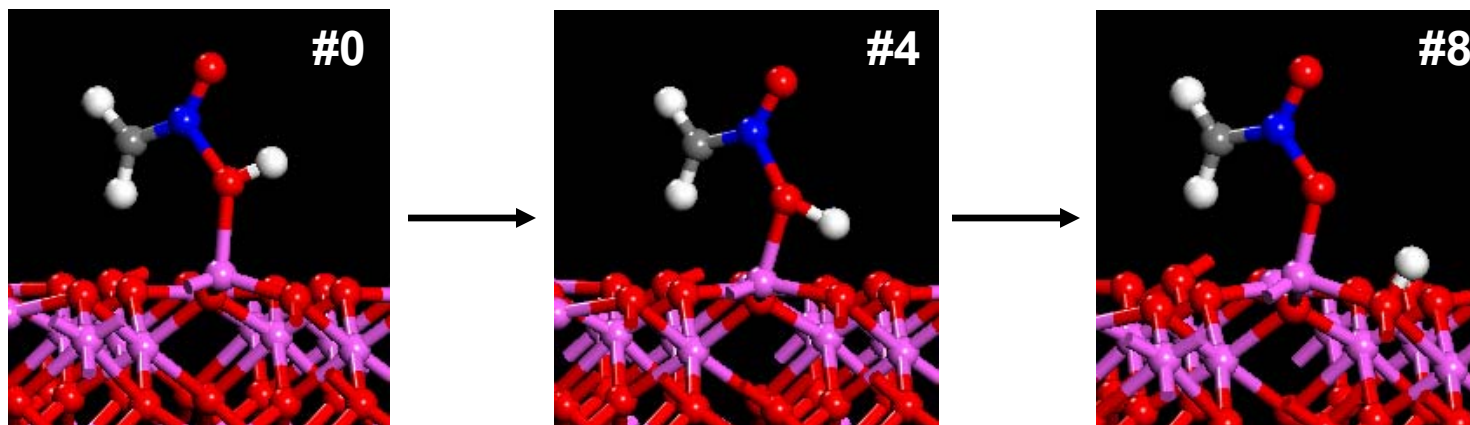
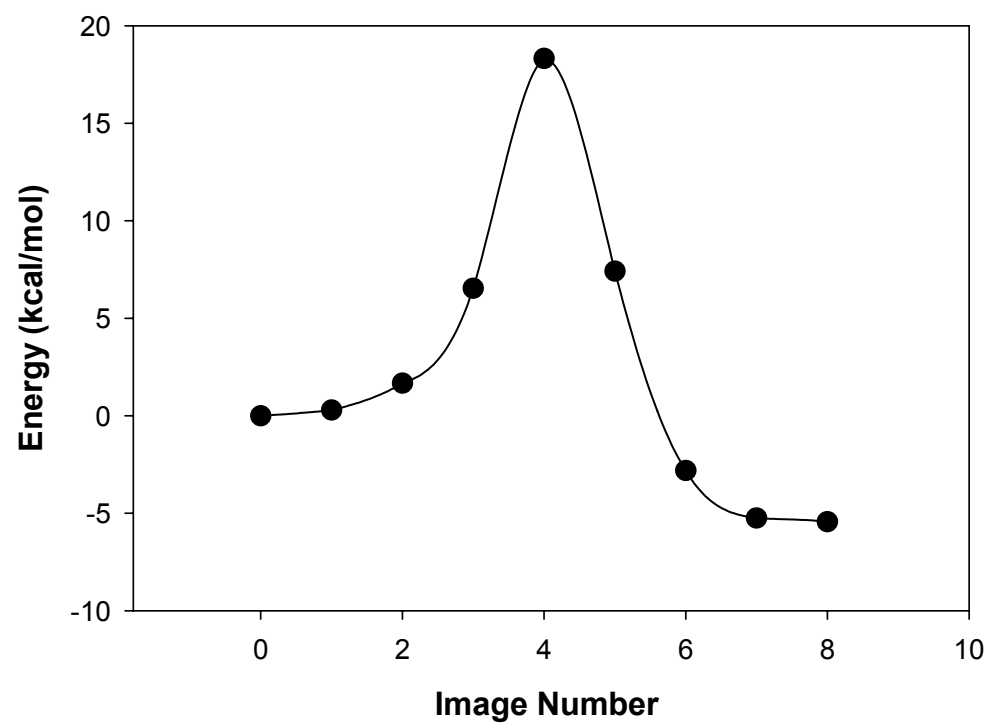


Fig. 9

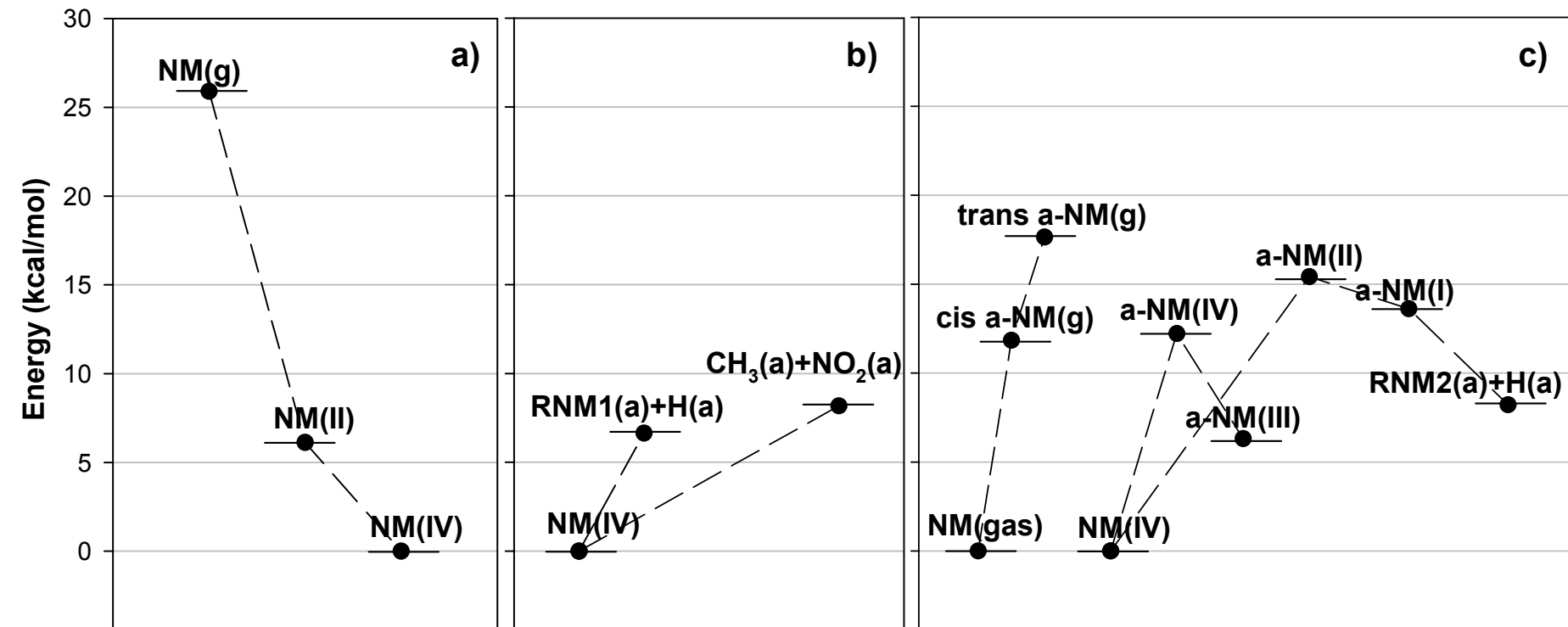
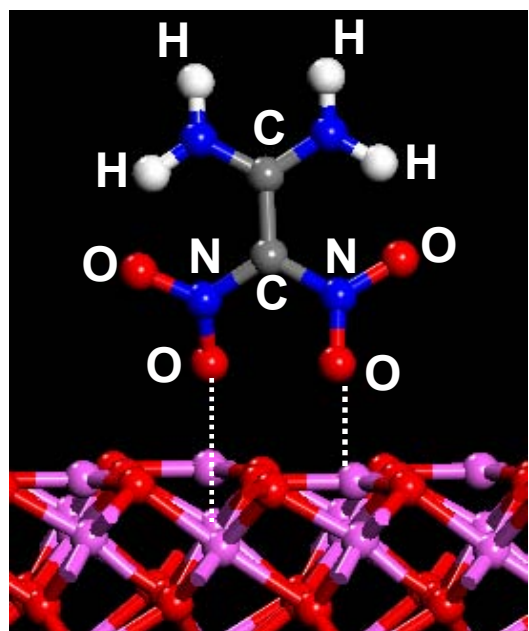
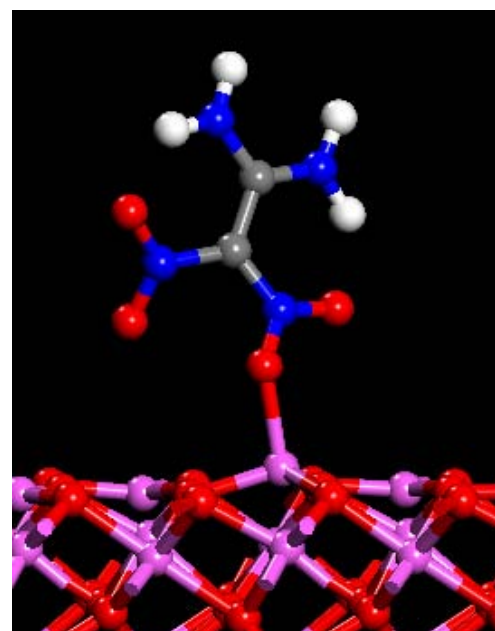


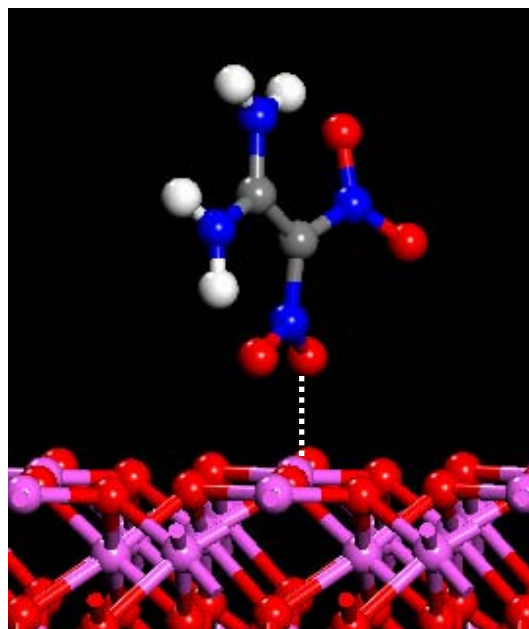
Fig. 10



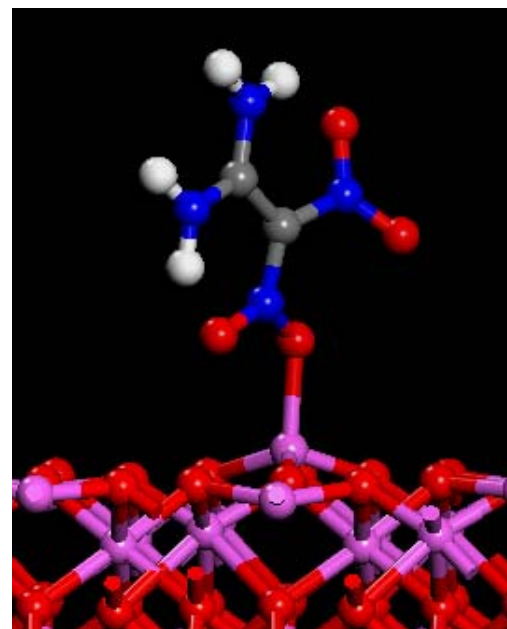
a1)



a2)



b1)



b2)

Fig. 11

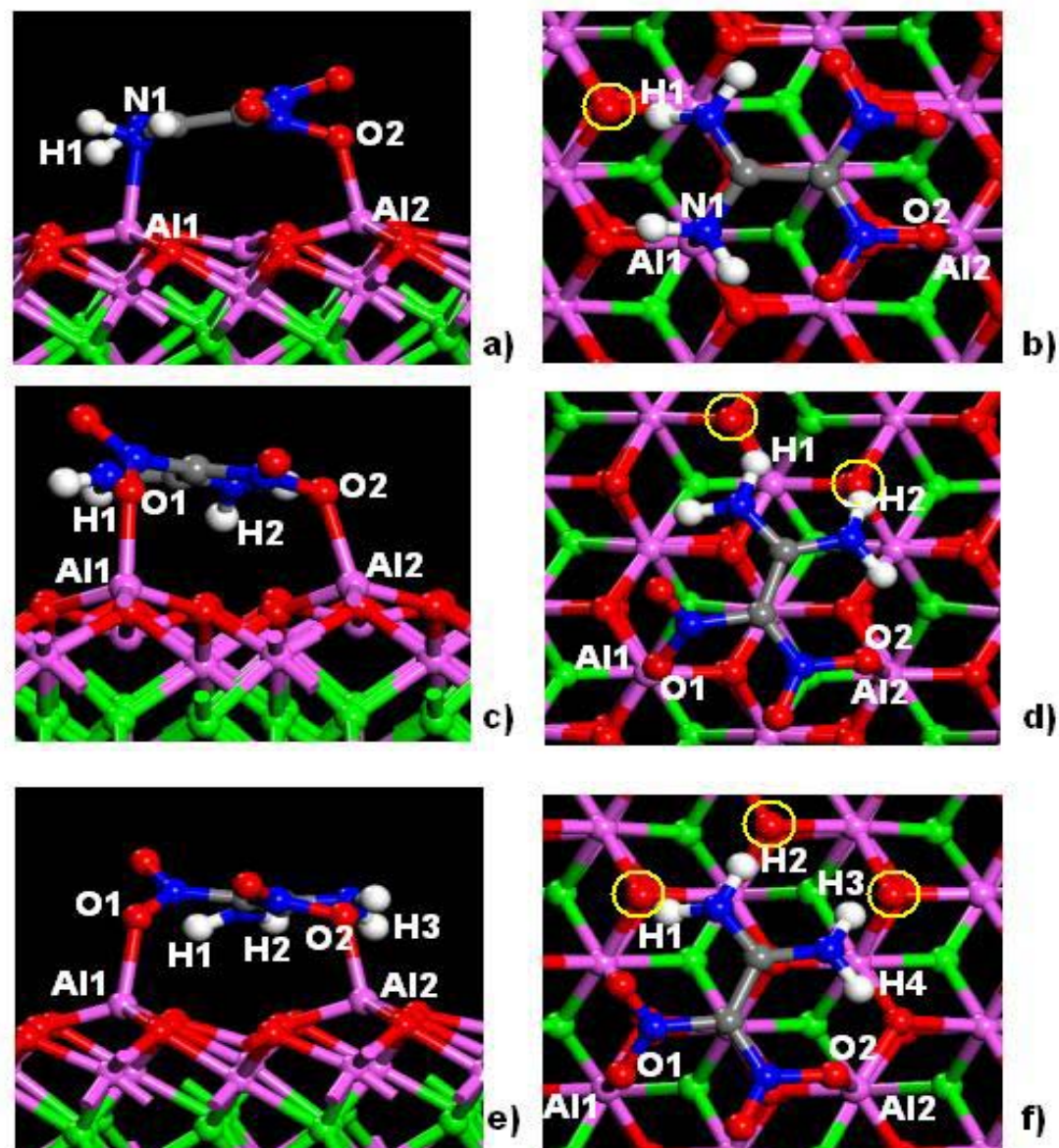


Fig. 12