

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

8 May 2003

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-130**
Jerry Boatz (AFRL/PRSP) et al., "First Principles Calculations of the Interaction of Nitro Compounds
with the Al (111) Surface"

DoD High Performance Computing Users Group Conf.
(Bellevue, WA, 9-13 June 2003) (Deadline = 09 June 2003)

(Statement A)

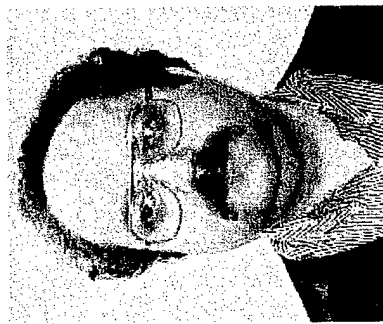
**First Principles Calculations of the Interaction
of Nitro Compounds with the
Al (111) Surface
DoD UGC, 9-13 Jun 03
Bellevue, WA**



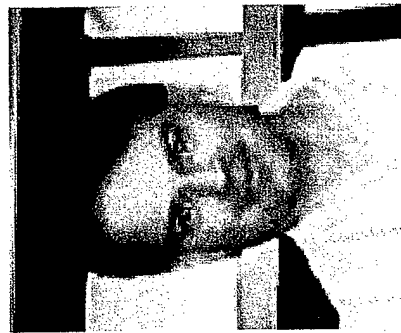
Jerry Boatz
Senior Research Chemist
Propulsion Directorate
Air Force Research Laboratory



Multiscale Simulations of High Energy Density Materials (MSoH) Challenge Project



Dan C. Sorescu*



Jerry Boatz**

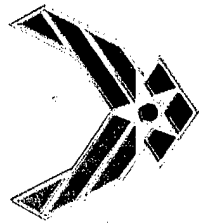


Donald L. Thompson***

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OUTLINE



1. Introduction

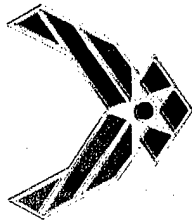
- Background on HEDM
- Payoffs

2. Theoretical Methods and benchmarks

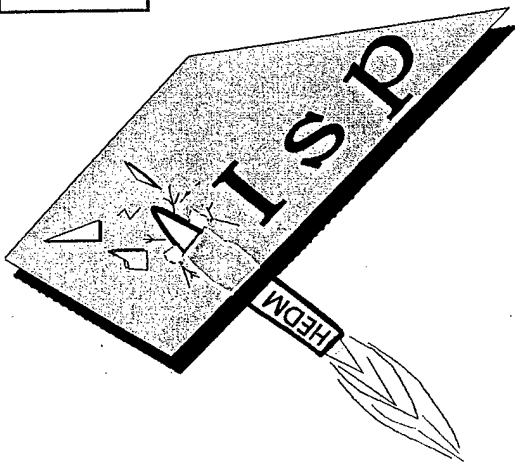
- Plane-wave DFT
- Molecular Dynamics

3. Results

4. Summary

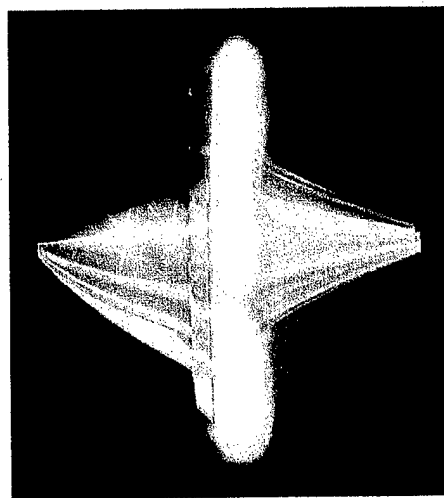
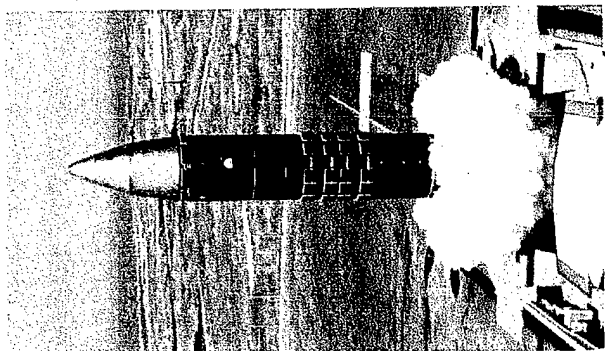
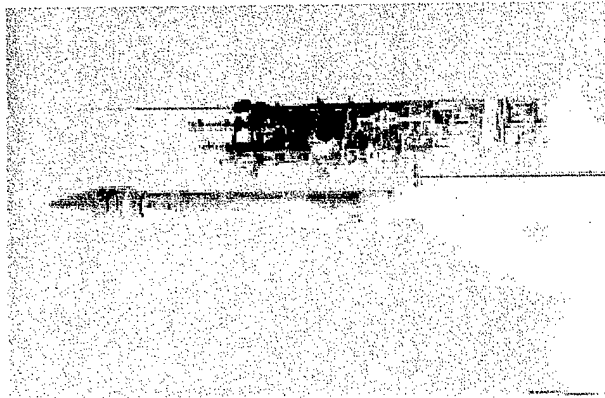
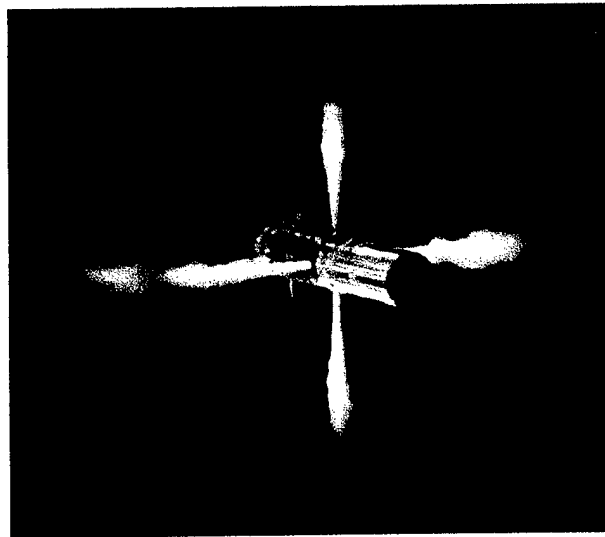


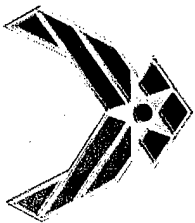
What We Are Trying To Do



Identify, develop, and transition new propellants and advanced concepts for propulsion applications

- Hydrocarbon fuels for liquid boost
- Liquid & solid oxidizers for boost and upper stages
- Monopropellants for spacecraft and upper stages
- Laser lightcraft for microsatellite and other applications

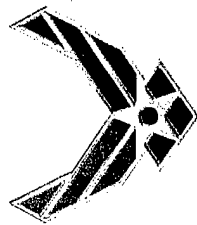




What Difference It Will Make

Vehicle Type	Baseline Vehicle	Propellant	Takeoff Mass (lb)	Payload Mass (lb)	Payload Mass (lb) With 10% Isp Increase
Two-stage ELV	Atlas II // Centaur D-1A	RP-1/LOX (Isp = 295 s) // LH2/LOX (Isp = 455 s)	360,000	12,500	15,600 (+25%)
SSTO RLV	Lockheed SSTO	LH2/LOX (Isp = 455 s)	1,900,000	40,000	68,000 (+70%)
Missile Defense Interceptor	Boost-Phase Interceptor	HTPB/Al/HMX (Isp = 270 s)	1,847	74	110 (+49%)

Our research is aimed at increasing propellant Isp by as much as 50%



How We Do What We Do

Propellant Discovery & Development



Employ a synergic blend of experimental, theoretical, and computational techniques derived from the disciplines of chemistry and physics

Experiments

Exploratory experiments

Identify target compounds

Calculate stability and performance

Theory & modeling

Develop new synthesis methods

Attempt synthesis on small scale

Calculate synthesis or decomposition routes

Measure properties & compare with predictions

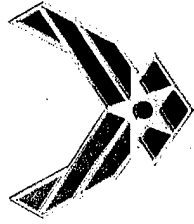
Characterize new materials

Model spectral fingerprints

Optimize synthesis, devise test methods

Scale up, formulate and test

Transition to Industry



MSoH: Concept

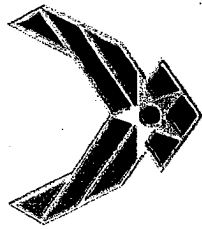


Atomistic level understanding of condensed phase properties of energetic materials

- which factors influence the phase transitions (e.g., the melting point of energetic crystals?
- what is the mechanism of phase stabilization in AN salts?
- how are the chemical properties of energetic materials influenced by chemisorption on metallic surfaces?

Technical tasks include

- a) Characterization of static, dynamic properties of AN, ADN salts
 - structural, thermodynamic, transport properties and phase transitions
- b) Investigation of KNO_3 -induced phase stabilization of ammonium nitrate (AN) salts
- c) Interactions between HEDM molecules and Al surfaces, nanoclusters.
 - how do surface/cluster interactions modify the chemical properties of HEDM?
 - RDX, HMX, FOX-7 (1,1-diamino-2,2-dinitroethylene)



MSoH Project Objectives



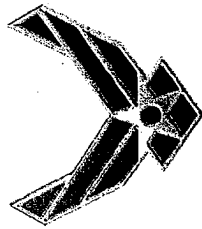
Objectives of the Current Computational Research Program

To identify the chemisorption mechanism of various nitro compounds on Al surface.

Particular important goals:

- a) to clarify if dissociative chemisorption can take place;**
- b) what type of species or radicals are formed on the surface.**

Limitations: temperature effects are not considered in the present set of calculations.



Computational Method : Ab Initio Total Energy Calculations

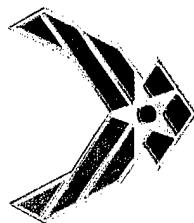


- Theoretical approach: spin polarized DFT with GGA and pseudopotential method.
- The occupied electronic orbitals are expanded in a plane-wave basis $\Psi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r})$ with reciprocal lattice vectors $\mathbf{G}$ limited by $\frac{\hbar^2 G^2}{2m} < E_{cut}$, $E_{cut}: 395 \text{ eV}$
Exchange-Correlation Functionals: PW91
- Pseudopotentials: Ultrasoft Vanderbilt-type
- K-point sampling: Monkhorst-Pack Special K-pts
- Electron Smearing Near Fermi Level with Extrapolation to $T=0$
VASP: Methfessel-Paxton Function, 0.2 eV min. width.



VASP: "Vienna Ab Initio Simulation Package",
J. Haffner, G. Kresse et al., Univ. of Vienna

ARL, ASC, and ERDC MSRCs

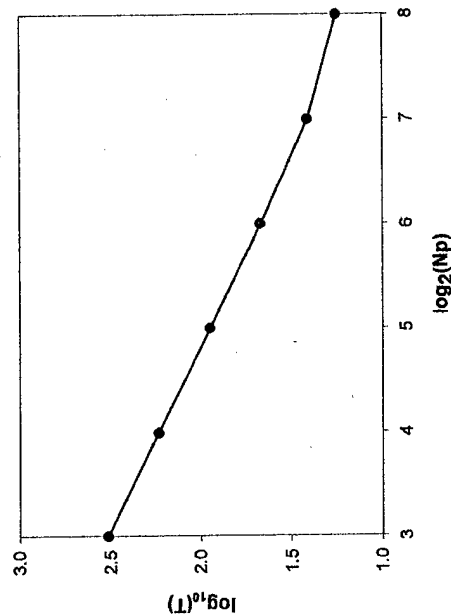


MSoH: Scalable CCM Software



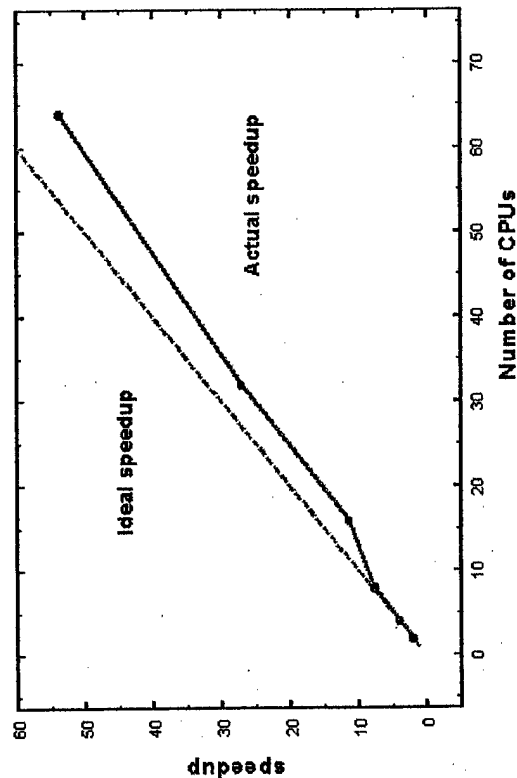
DL_POLY_2.0

Run on Cray T3E



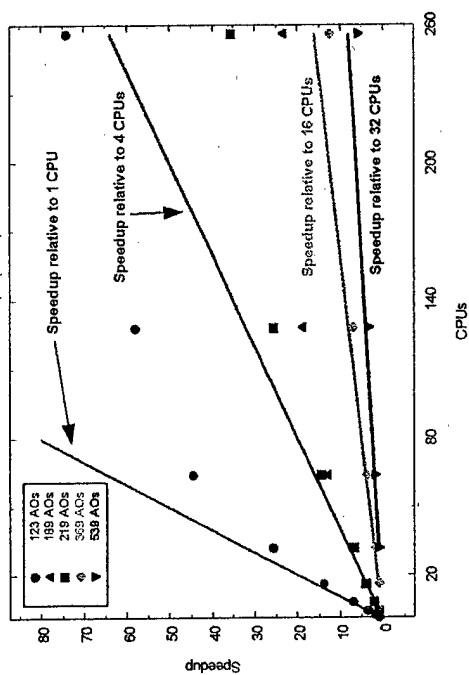
CASTEP

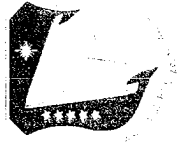
Run on SGI O3K



GAMESS

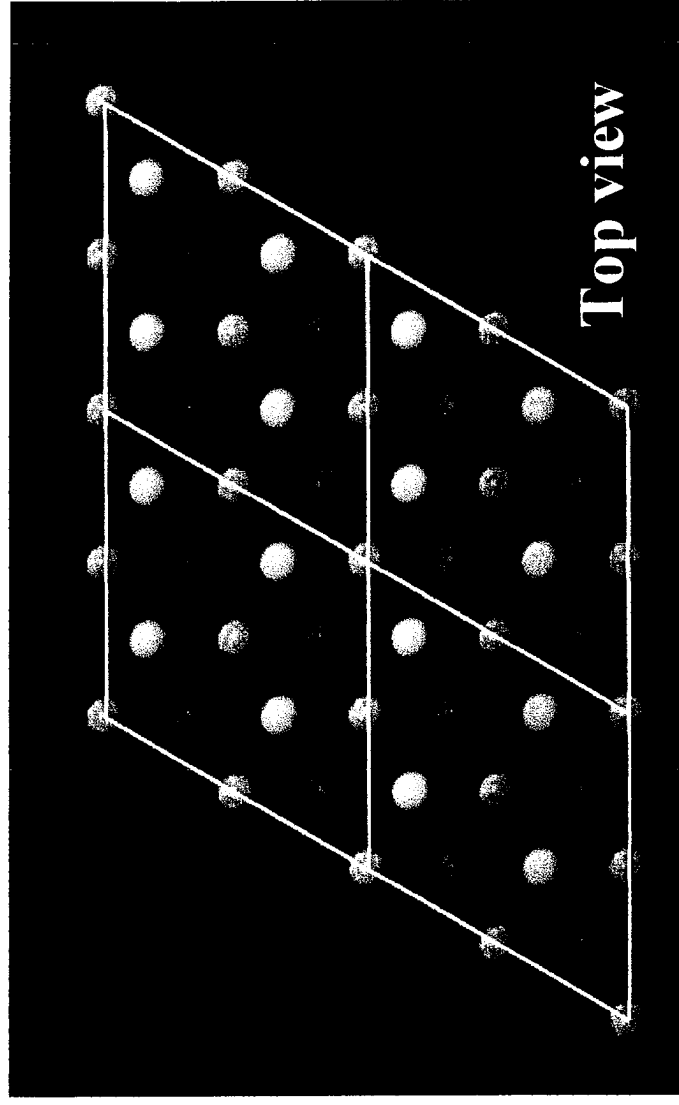
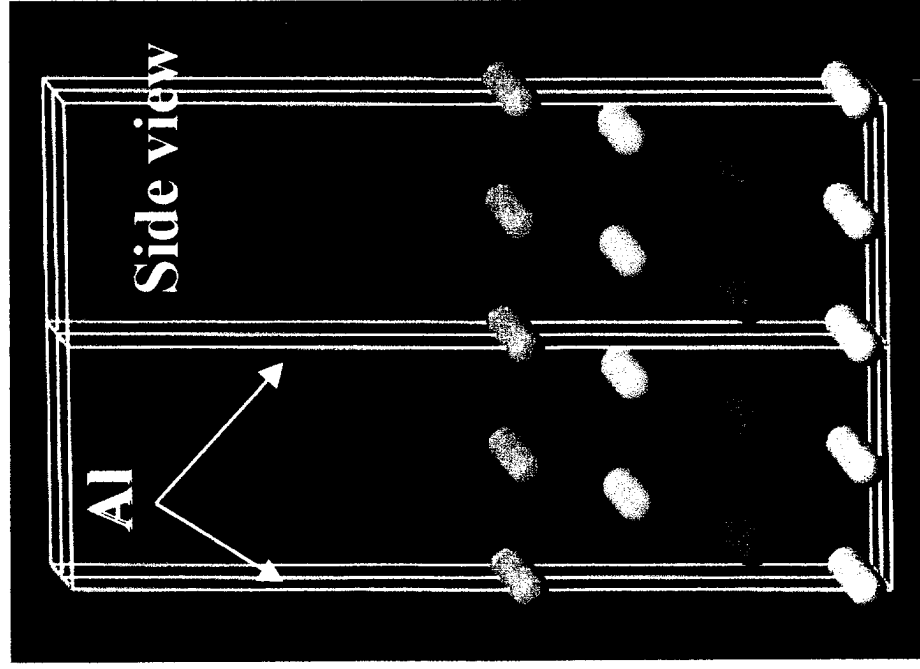
MP2 Gradient Scalability Test
Silicocene molecule, Si(C5H5)2

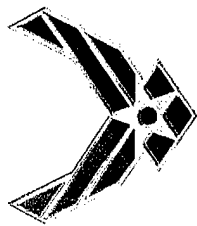




Al(111) Slab Model

Al(111)- (3x3) surface units
slab model with 4 layers
(36 Al atoms), 3D periodic
boundary conditions

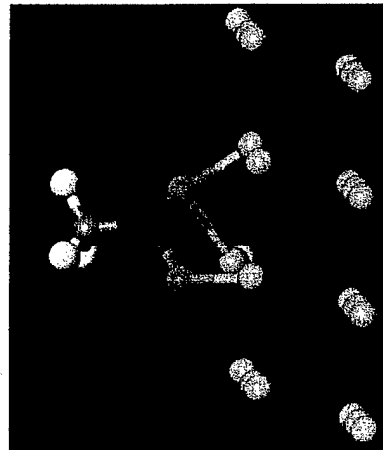
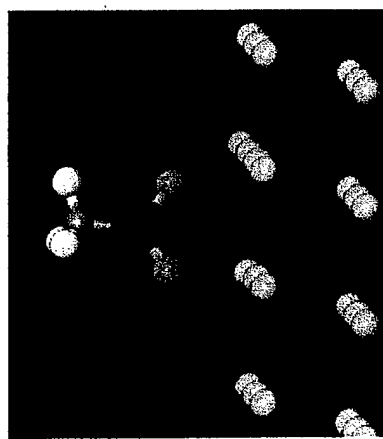




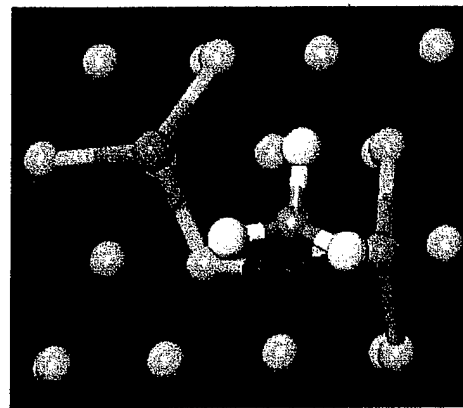
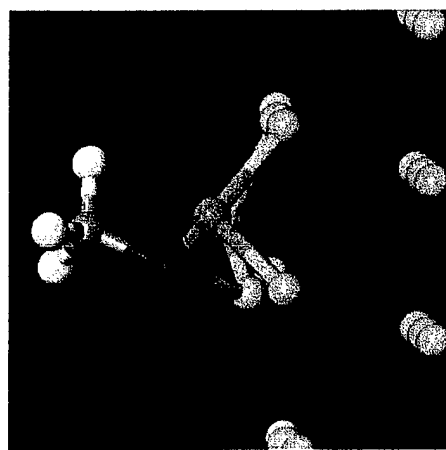
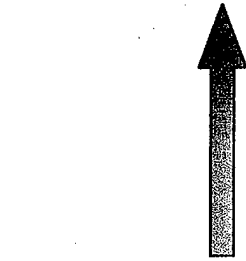
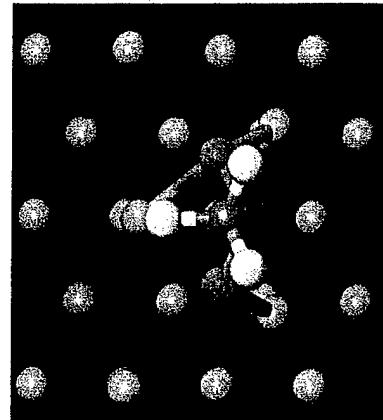
Chemisorption of Nitromethane on Al(111)



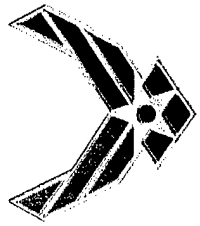
Initial configuration



Optimized configuration
side view

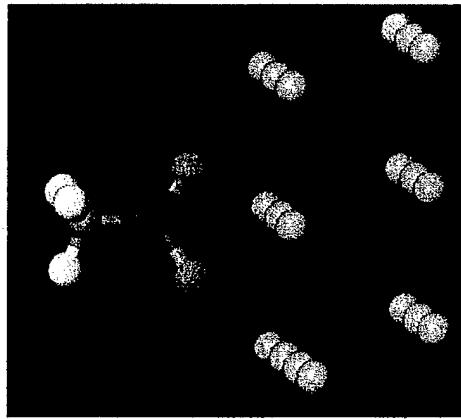


Formation of strong Al-O bonds; deformations of NM molecule

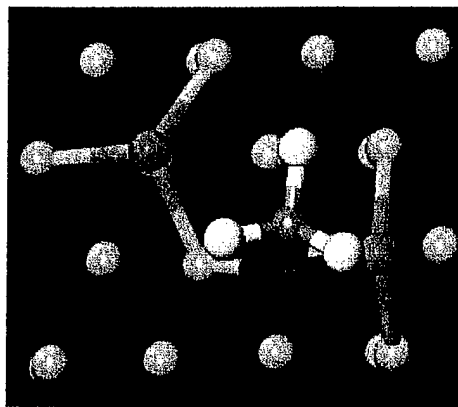
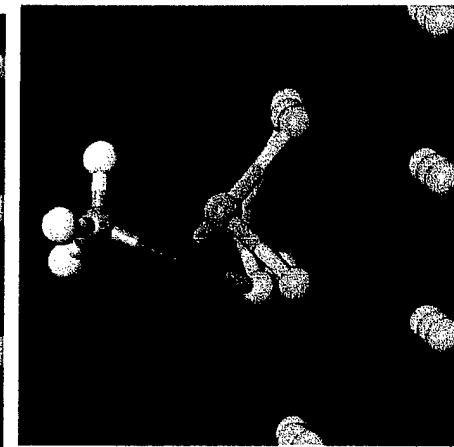
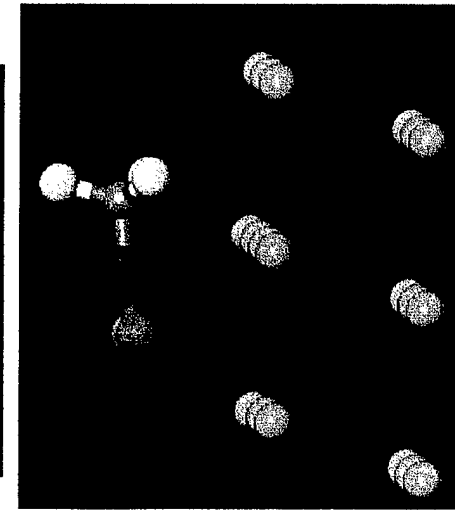
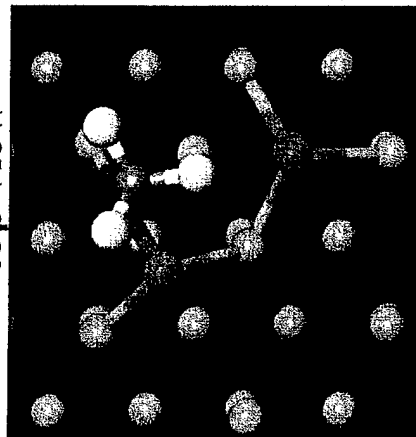
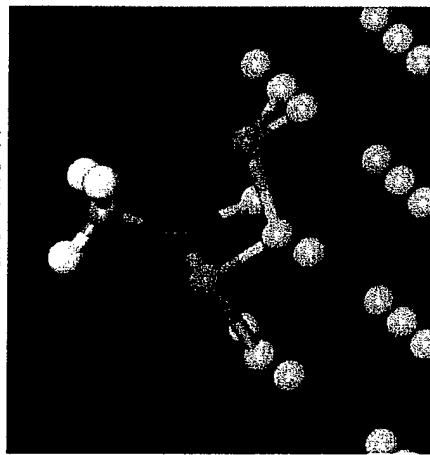


Dissociative Chemisorption of Nitromethane

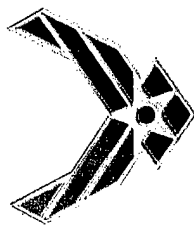
Initial configuration



Optimized configuration
side view

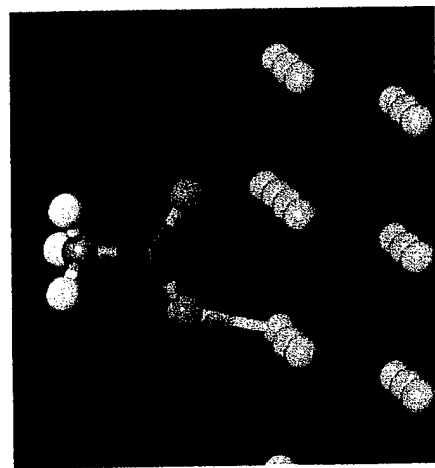


* Dissociation of one O atom, oxidation of Al surface atoms.

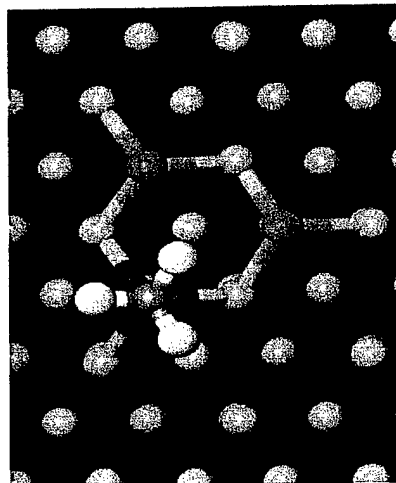
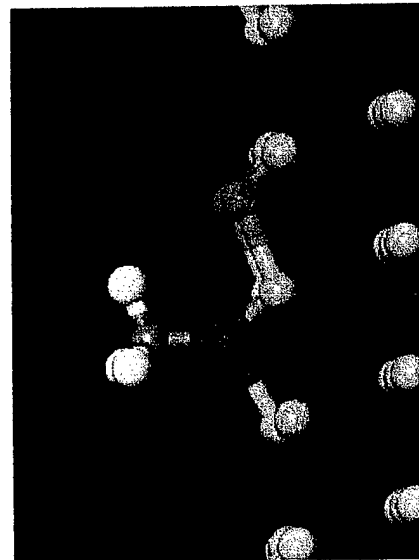
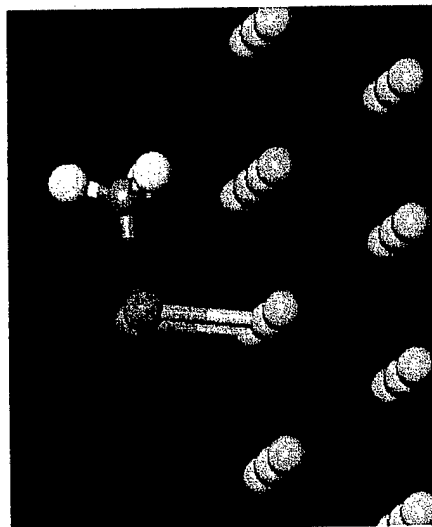
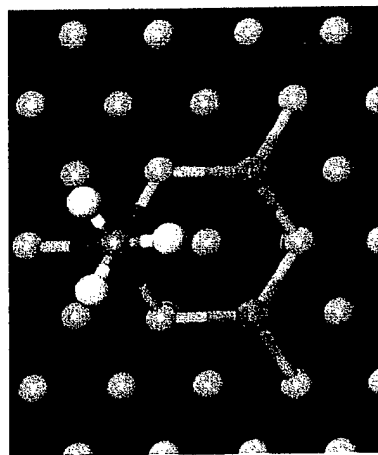
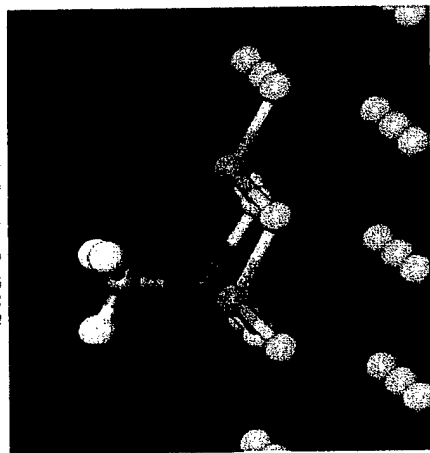


Dissociative Chemisorption of Nitromethane

Initial configuration



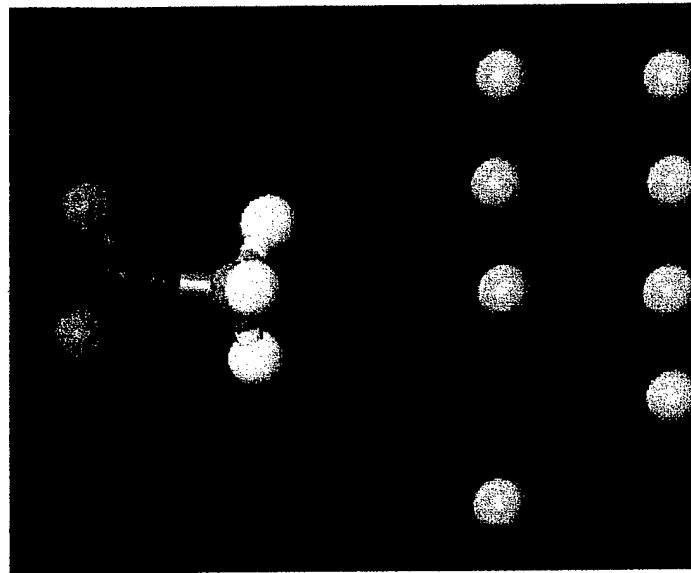
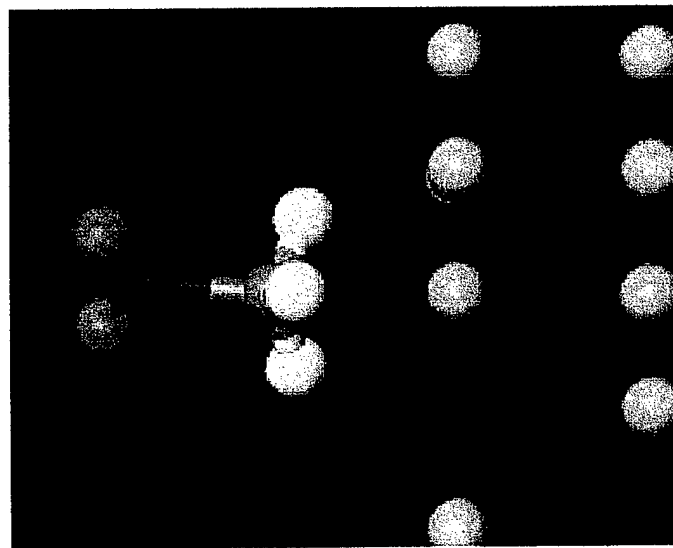
Optimized configuration
side view



*** Dissociation of both O atoms, oxidation of Al surface atoms.**

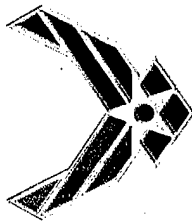


*There are some initial configurations for
which nitromethane does not chemisorb*

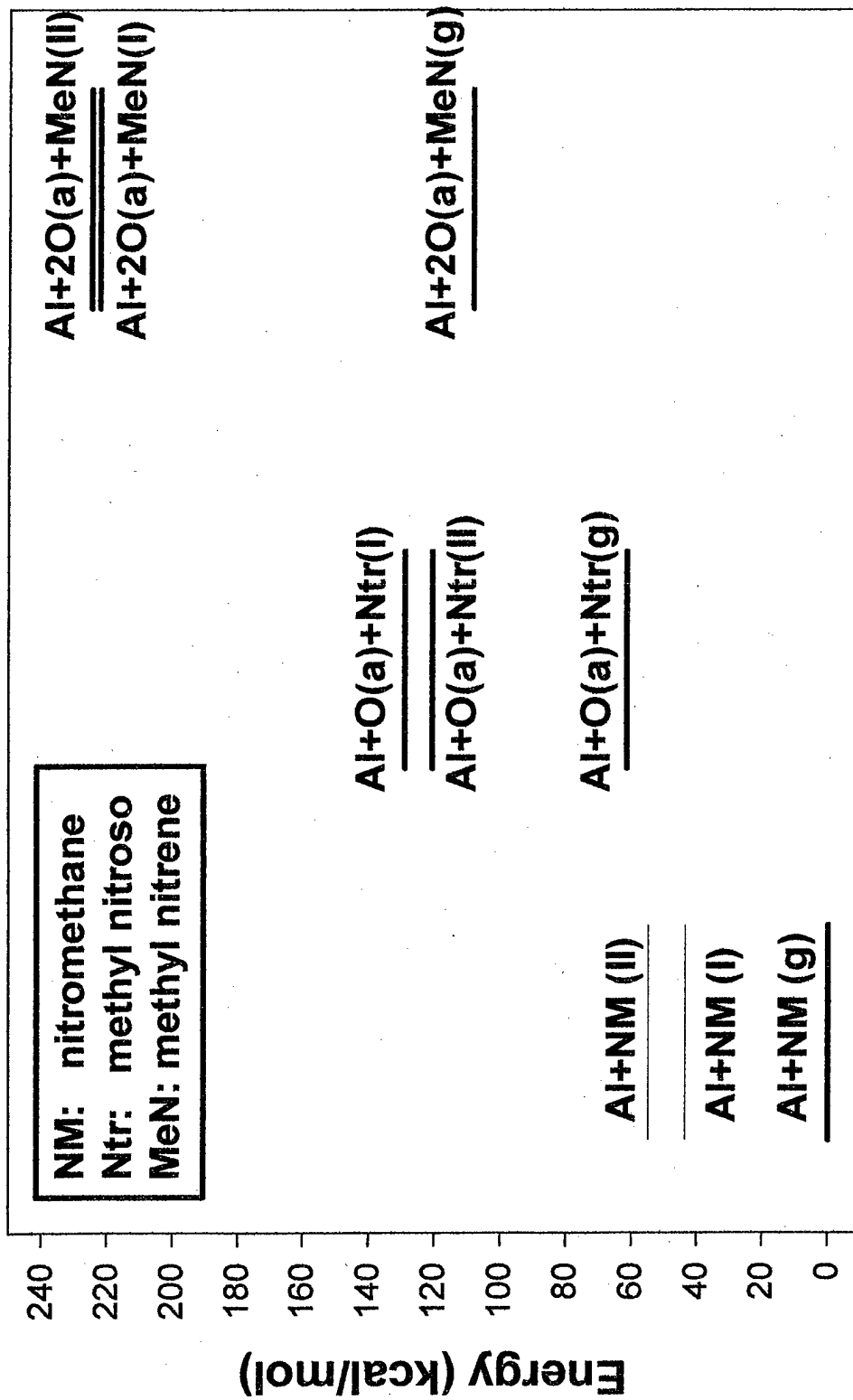


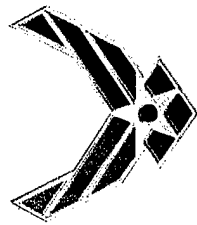
Initial configuration

Final configuration



Adsorption Energies of Nitromethane

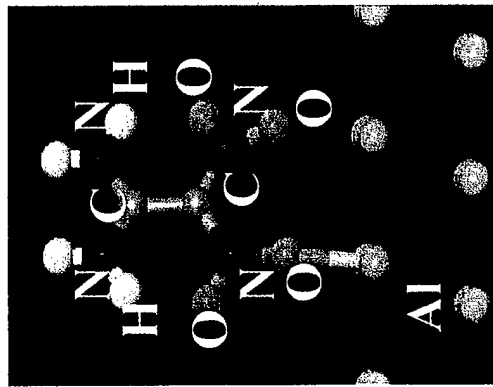




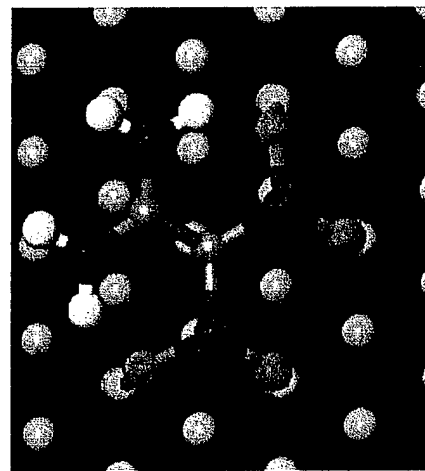
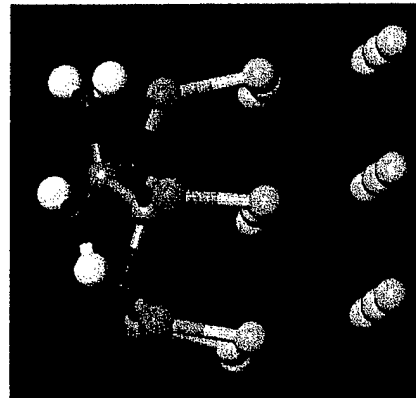
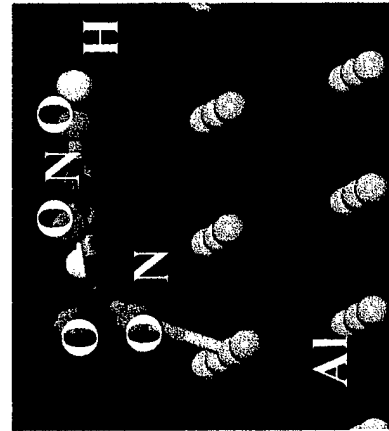
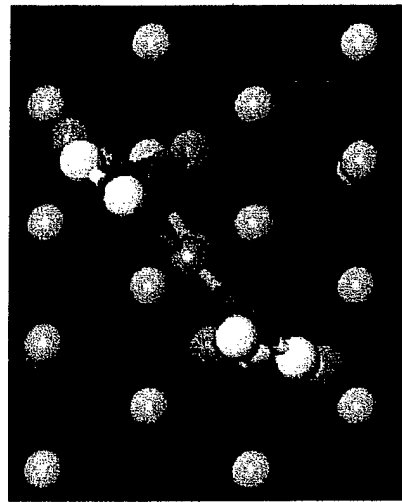
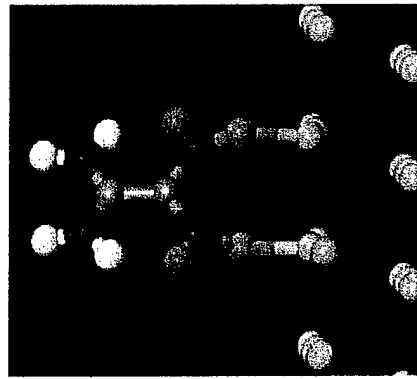
Chemisorption of FOX-7 on Al(111)



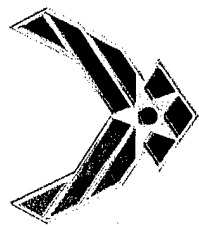
Initial configuration



Optimized configuration
side view



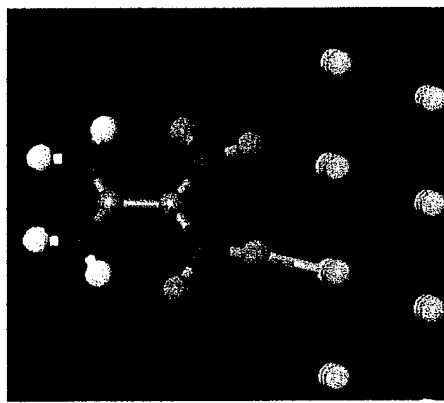
Formation of strong Al-O bonds; deformations of FOX-7



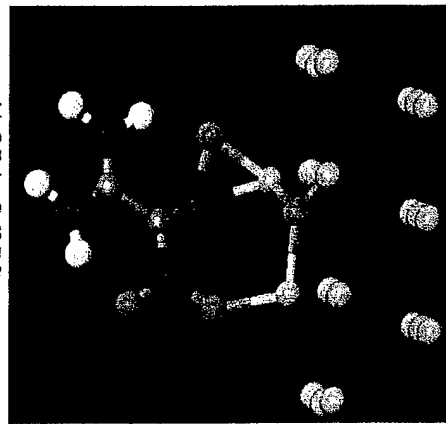
Dissociative Chemisorption of FOX-7



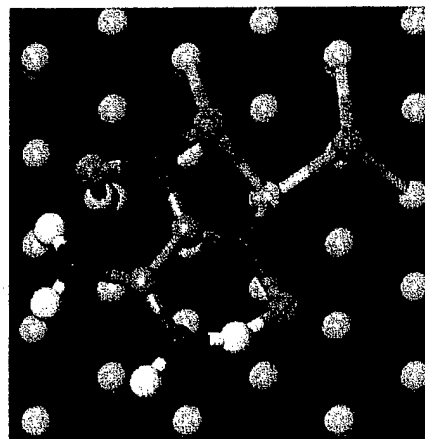
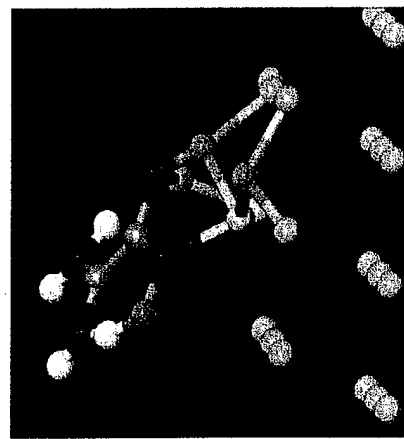
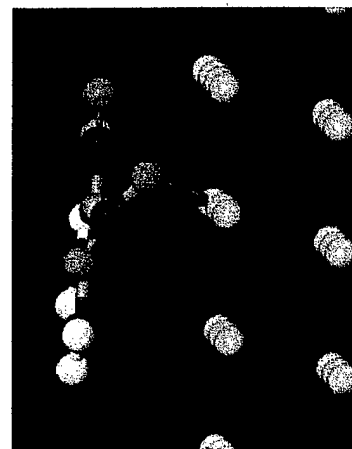
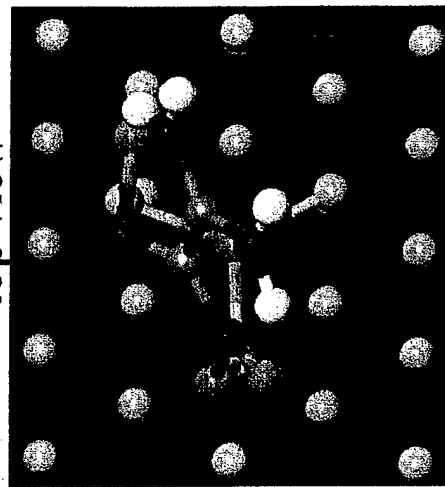
Initial configuration



Optimized configuration
side view



top view



*** Dissociation of one O atom, oxidation of Al surface atoms.**

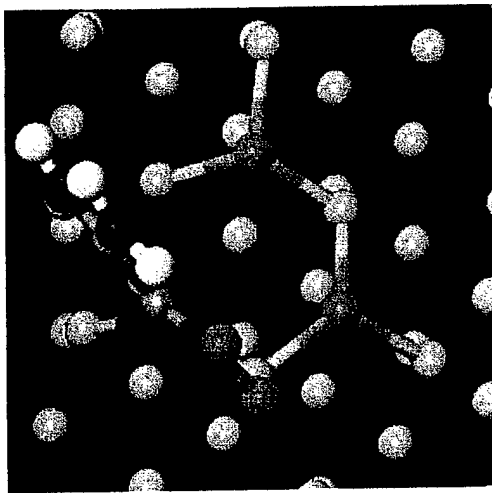
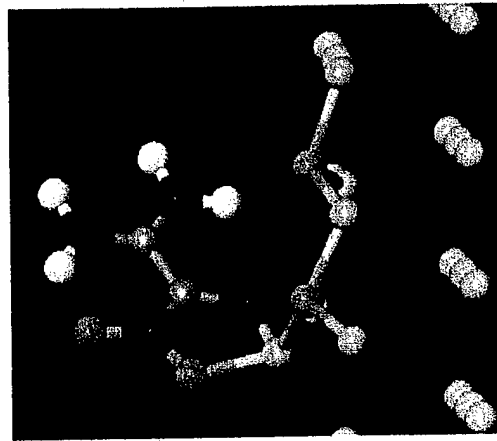
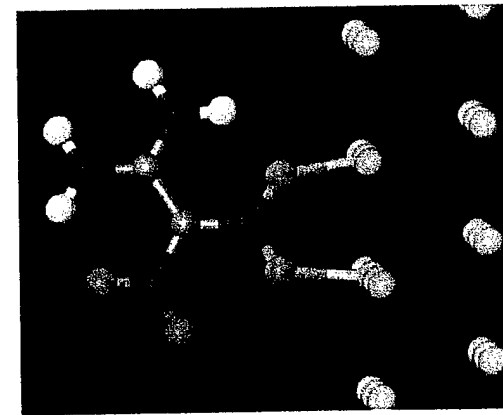


Dissociative Chemisorption of FOX-7



Initial configuration

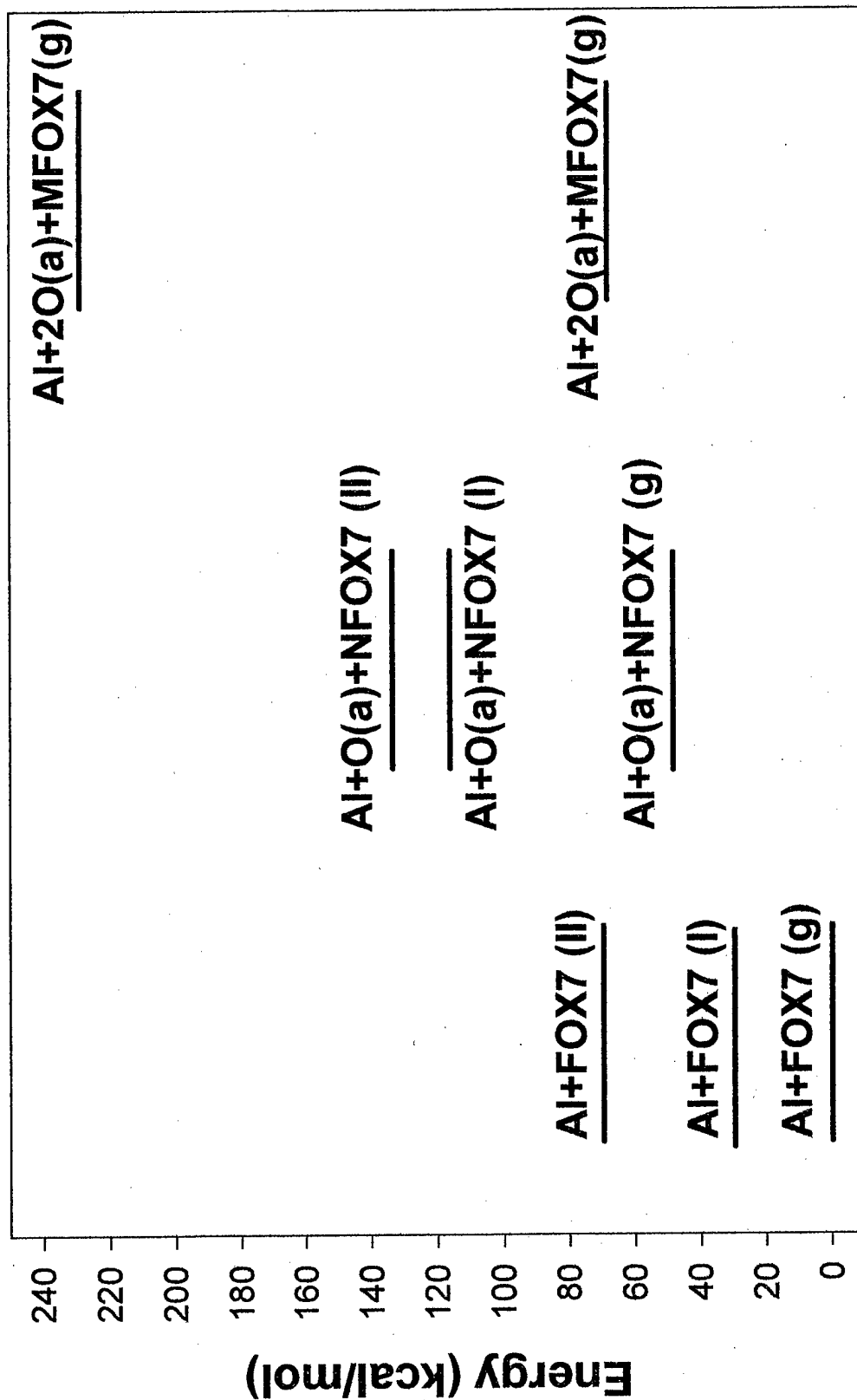
Optimized configuration
side view



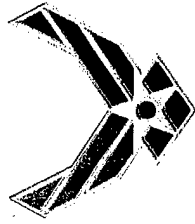
*** Dissociation of both O atoms, oxidation of Al surface atoms.**



Adsorption Energies of FOX-7



Computational requirements: 220,000 hours on ERDC Cray T3E, ARL SGI 3800



Conclusions

Both non-dissociative and dissociative interactions are found

- (1) non-dissociative formation of N-O-Al bonds
- (2) complete dissociation of one or two O atoms with subsequent formation of Al_3O "cap" sites.

Non-dissociative adsorption energies are 30-70 kcal/mol

Adsorption energies for single O-atom dissociation are 110-130 kcal/mol

Adsorption energies for double O-atom dissociation are 220-230 kcal/mol

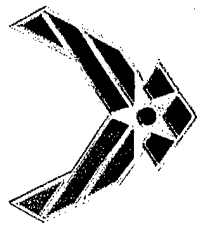
Adsorption energies of the nitroso and nitrene fragments are 60-80 kcal/mol and 110-160 kcal/mol, respectively

Neither NM or FOX-7 completely passivate the aluminum surface against oxidation

Dissociative adsorption is competitive with O_2 adsorption (105 kcal/mol)

Chemisorption of nitroso and nitrene fragments may sterically and/or energetically inhibit growth of aluminum oxide overcoat

Formation of Al-O bonds appears to be general process in nitro compounds



Summary & Future Directions



Summary

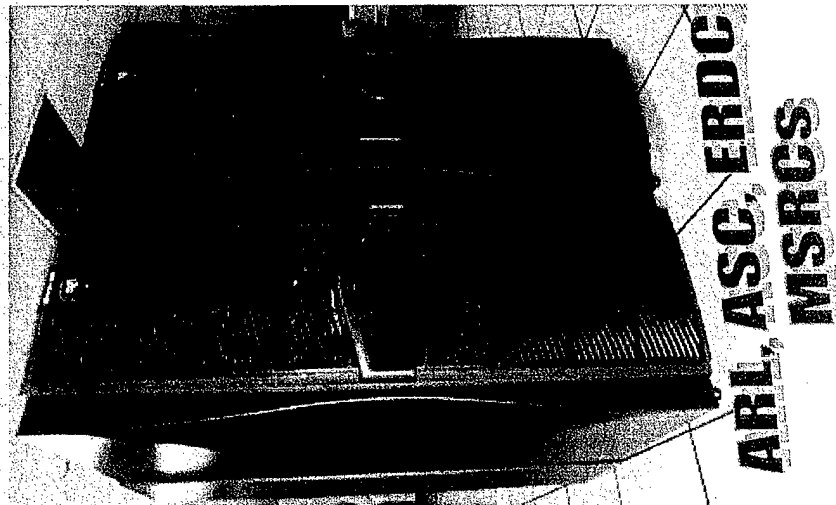
Interactions and adsorption energies of nitromethane and FOX-7 with the aluminum (111) surface have been calculated.

Multiple starting configurations have been examined (vertical & horizontal wrt metal surface; interactions with fcc, on-top, and hcp surface sites)

Future Directions

Interactions of NM and FOX-7 on aluminum oxide surface

Interactions of ammonium nitrate (AN) on Al (111)



DOD HPCMP

Challenge Project Award

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