

REPORT DOCUMENTATION PAGE

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attached

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

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AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

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Unclassified Unclassified Unclassified

A

Leilani Richardson
19b. TELEPHONE NUMBER
(include area code)
(661) 275-5015

2303MCP

MEMORANDUM FOR PRS (In-House Contractor Publication)

FROM: PROI (STINFO)

17 May 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-VG-2002-116
Jerry Boatz (PRSP) et al., "First Principles Calculation of the Chemisorption Properties of Nitro-containing Molecules on the Al(111) Surface (Multiscale Simulations of High Energy Density Materials Challenge Project)" (Viewgraphs)

DoD Users Group Conference
(Austin, TX, 10-14 June 2002) (Deadline: 07 June 2002)

(Statement A)

- 1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.

Comments: _____

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- 2. This request has been reviewed by the Public Affairs Office for: a.) appropriateness for public release and/or b) possible higher headquarters review.

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- 4. This request has been reviewed by PR for: a.) technical accuracy, b.) appropriateness for audience, c.) appropriateness of distribution statement, d.) technical sensitivity and economic sensitivity, e.) military/national critical technology, and f.) data rights and patentability

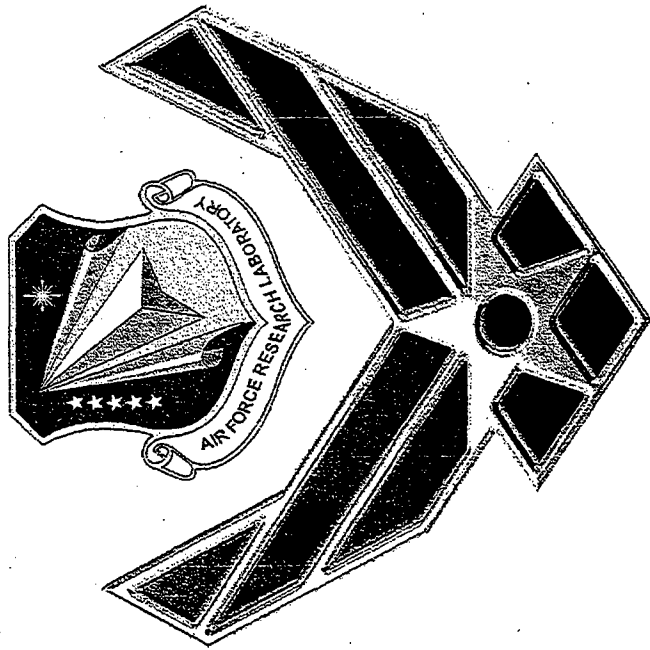
Comments: _____

APPROVED/APPROVED AS AMENDED/DISAPPROVED

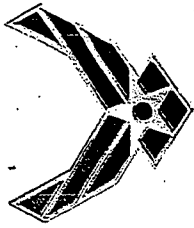
PHILIP A. KESSEL Date
Technical Advisor
Space and Missile Propulsion Division

CC 02-116

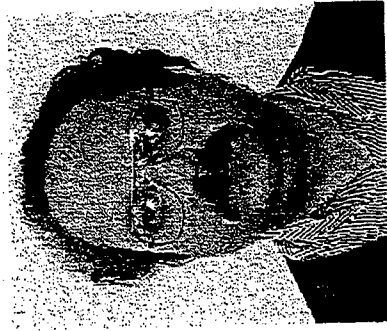
**First Principles Calculations of
of Nitro Compounds with the
Al (111) Surface
DoD UGC, 10-14 Jun 02
Austin, TX**



**Jerry Boatz
Senior Research Chemist
Propulsion Directorate
Air Force Research Laboratory**



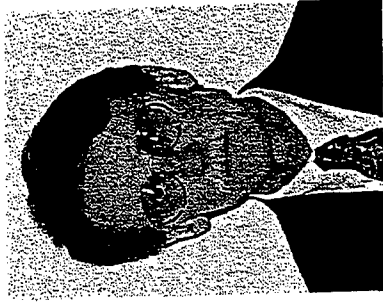
Multiscale Simulations of High Energy Density Materials (MSoH) Challenge Project



Dan C. Sorescu*



Jerry Boatz**

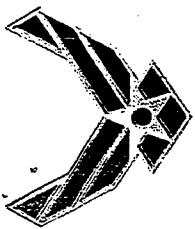


Donald L. Thompson***

* National Energy Technology Laboratory, Pittsburgh, PA 15236

** Air Force Research Laboratory, Edwards AFB, CA 93524

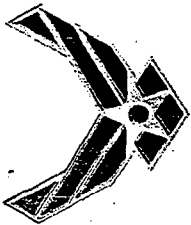
*** Oklahoma State University, Dept. of Chemistry, Stillwater, OK 74078



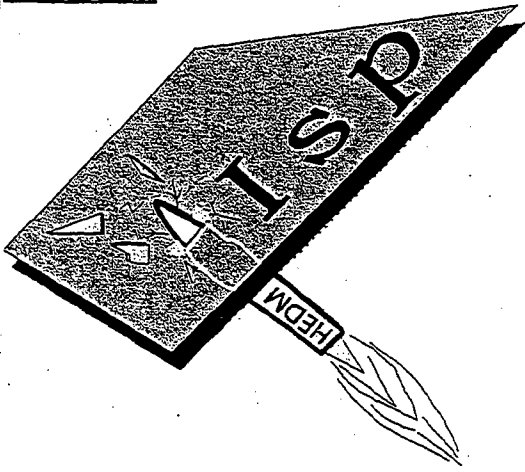
OUTLINE



- 1. Introduction**
 - Background on HEDM
 - Payoffs
- 2. Theoretical Methods and benchmarks**
 - Plane-wave DFT
 - Molecular Dynamics
- 3. Results**
- 4. Summary**

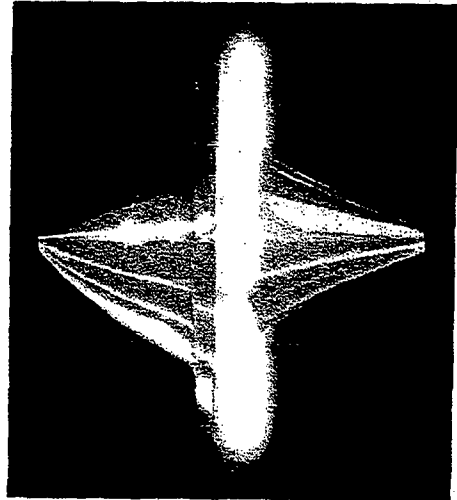
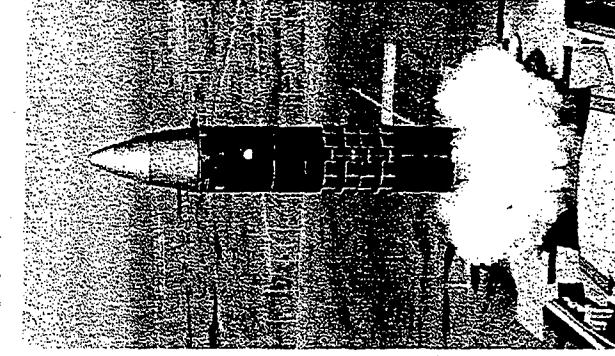
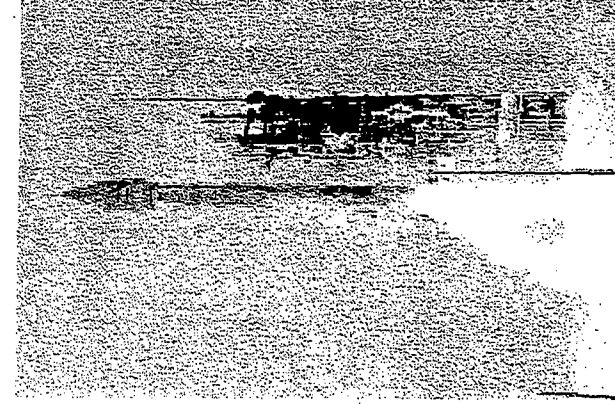
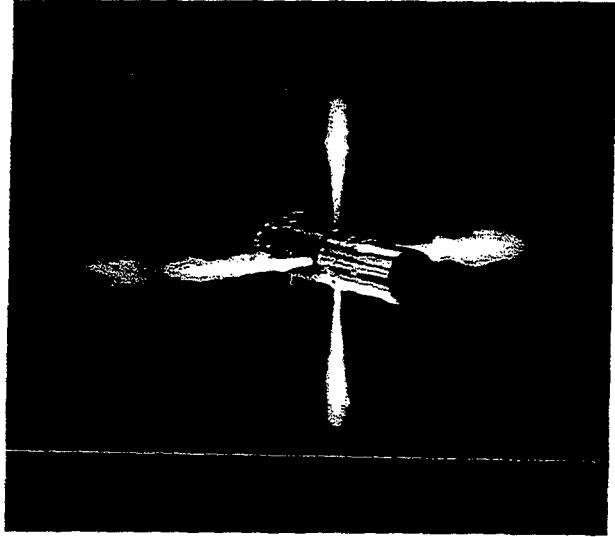


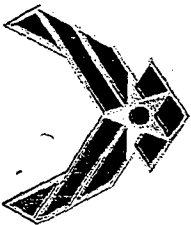
What We Are Trying To Do



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
- Cryogenic propellants for upper stages
- Laser lightcraft for microsattellite and other applications



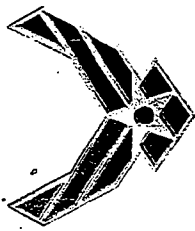


What Difference It Will Make



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%)

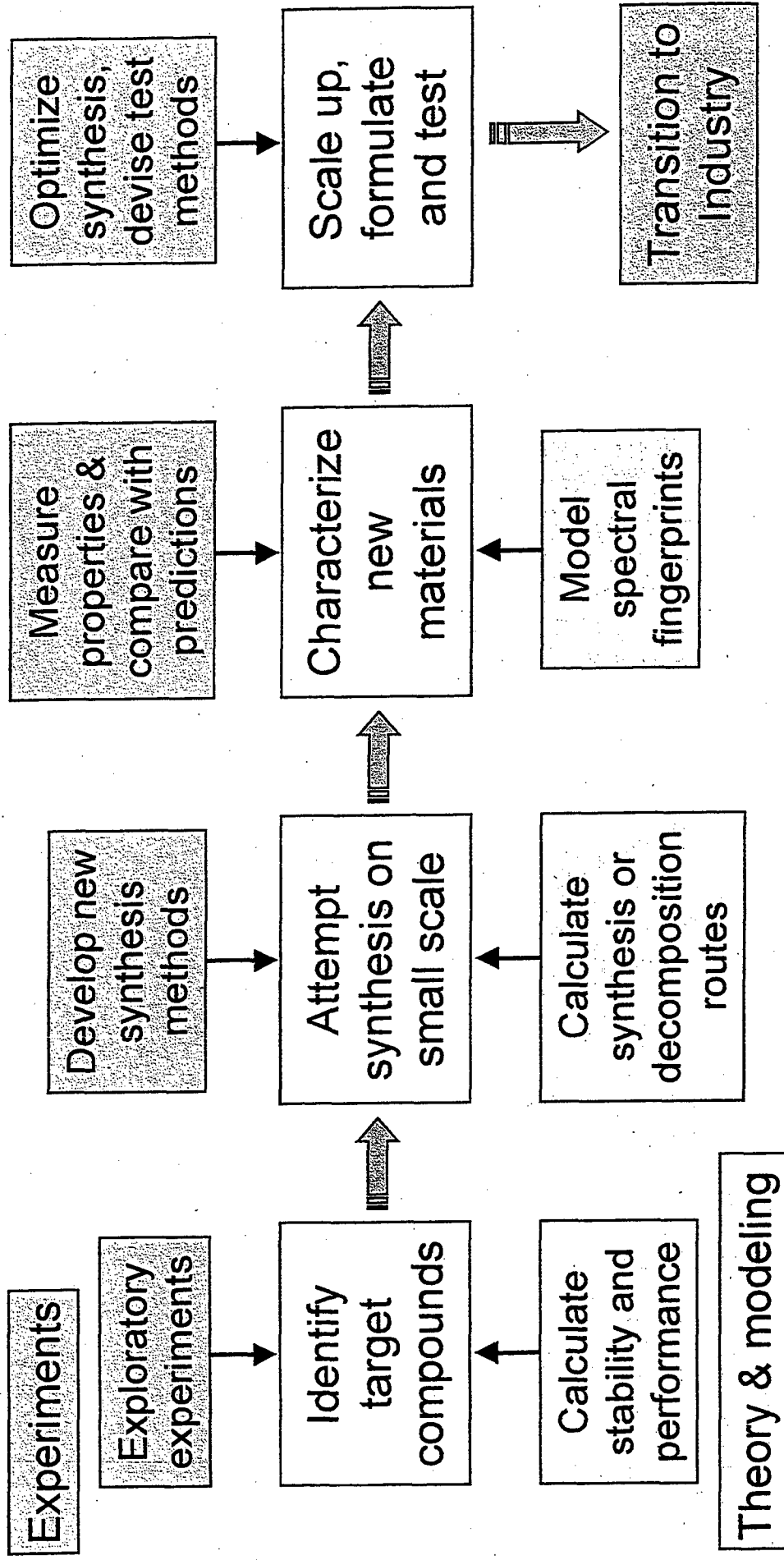
Our research is aimed at increasing propellant Isp by as much as 50%

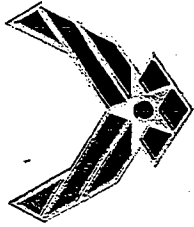


How We Do What We Do Propellant Discovery & Development



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





MSOH: Concept

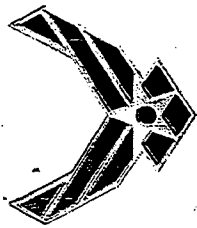


Atomistic level understanding of condensed phase properties of energetic materials

- 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



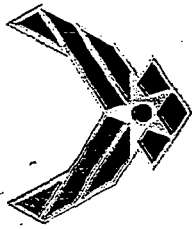
Objectives of the Current Computational Research Program

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.

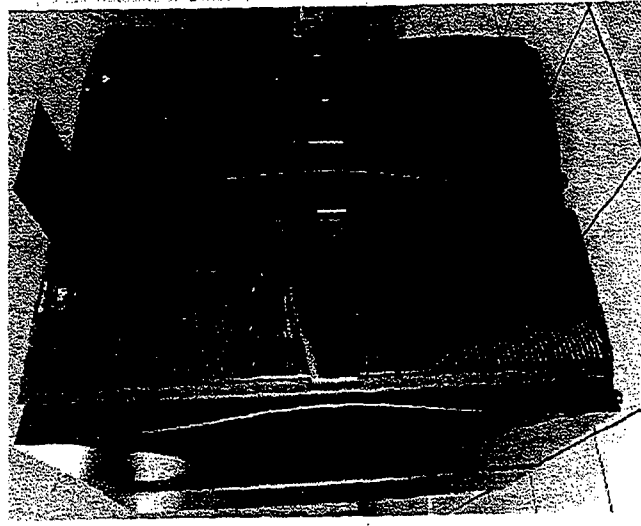
Limitations: temperature effects are not considered in the present set of calculations.



Computational Method : Ab Initio Total Energy Calculations



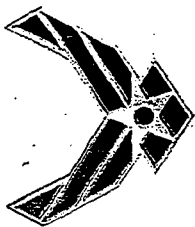
- Theoretical approach: spin polarized DFT with GGA and pseudopotential method.
- The occupied electronic orbitals are expanded in a plane-wave basis $\Psi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r})$ with reciprocal lattice vectors \mathbf{G} limited by $\frac{\hbar^2 \mathbf{G}^2}{2m} < E_{cut}$, $E_{cut}: 396 \text{ eV}$
- Exchange-Correlation Functionals: PW91
- Pseudopotentials: Ultrasoft Vanderbilt-type
- K-point sampling: Monkhorst-Pack Special K-pts
- Electron Smearing Near Fermi Level with Extrap. to $T=0$
- VASP: Methfessel-Paxton Function, 0.1 eV min. width.



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

DOD HPC

ARL MSRC and NAVO MSRC

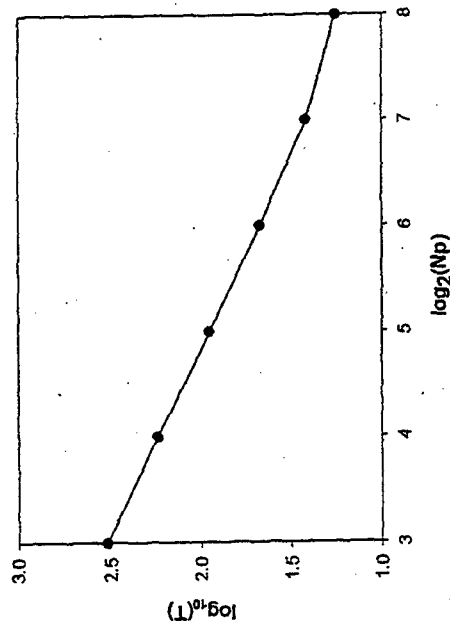


MSOH: Scalable CCM Software



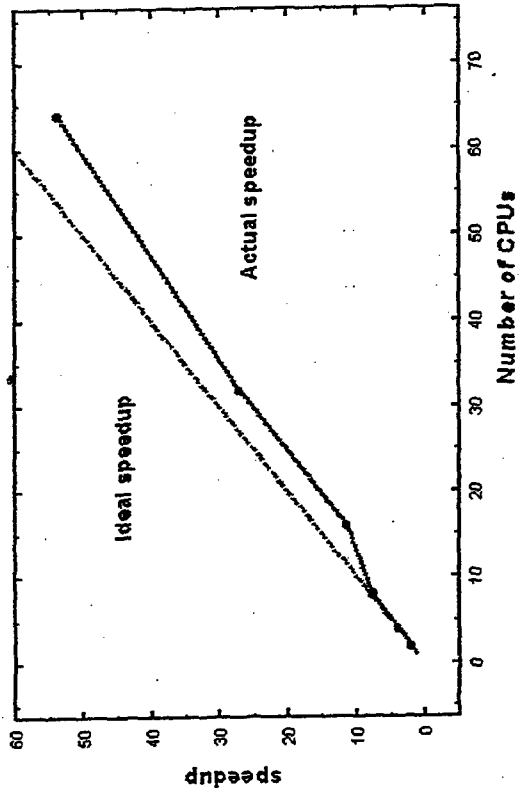
DL_POLY_2.0

Run on Cray T3E



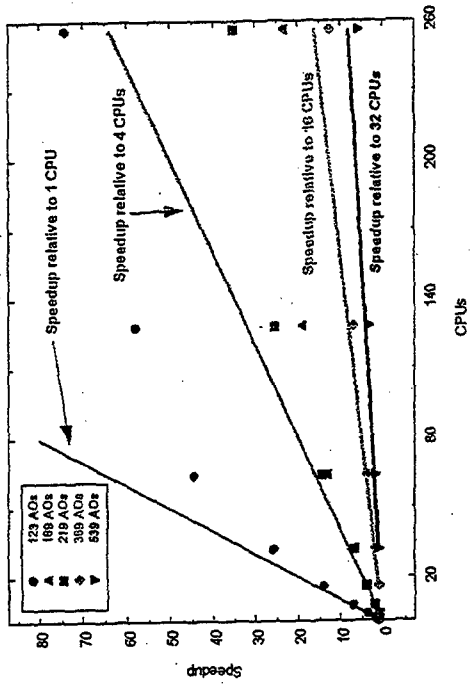
CASTEP

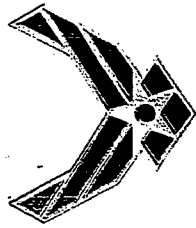
Run on SGI O3K



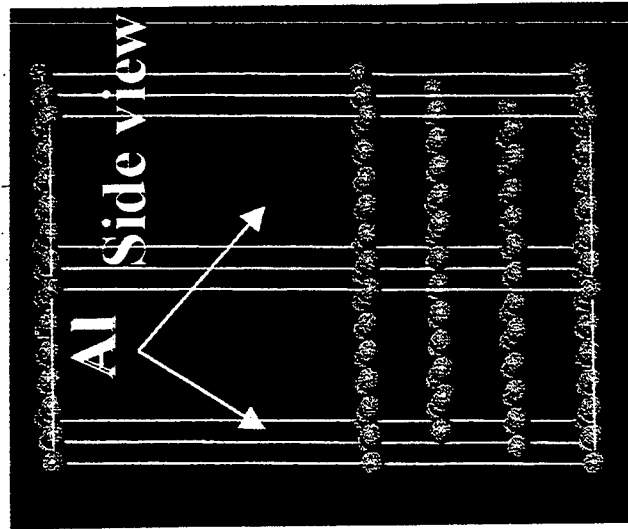
GAMESS

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



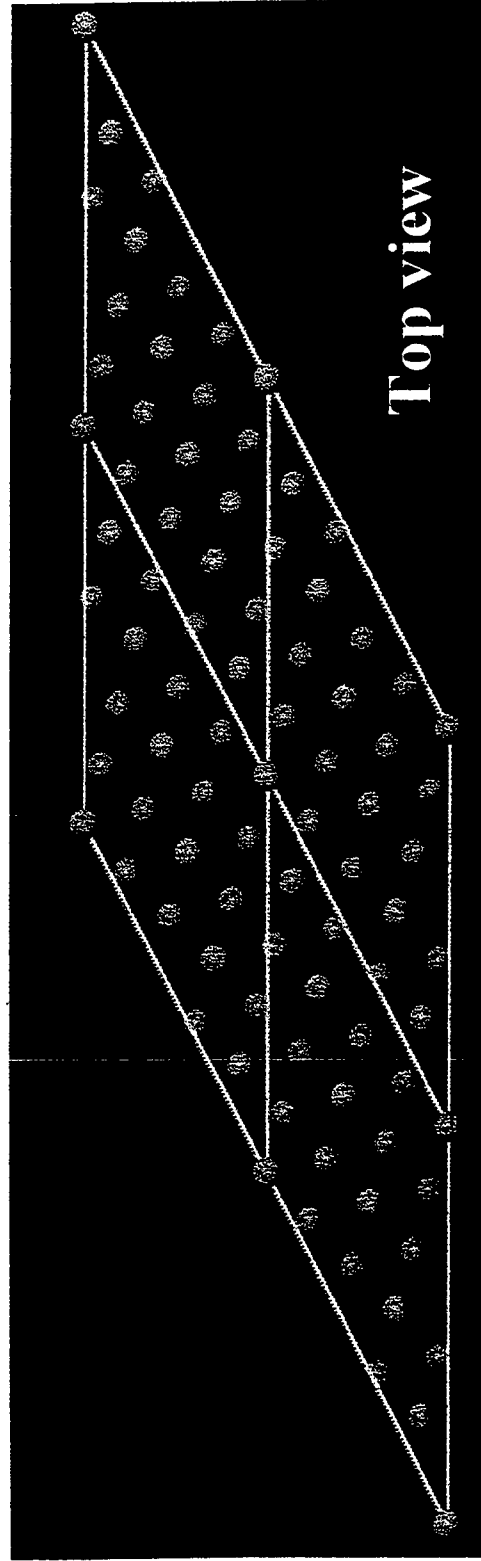


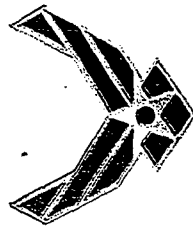
Al(111) Slab Model (I)



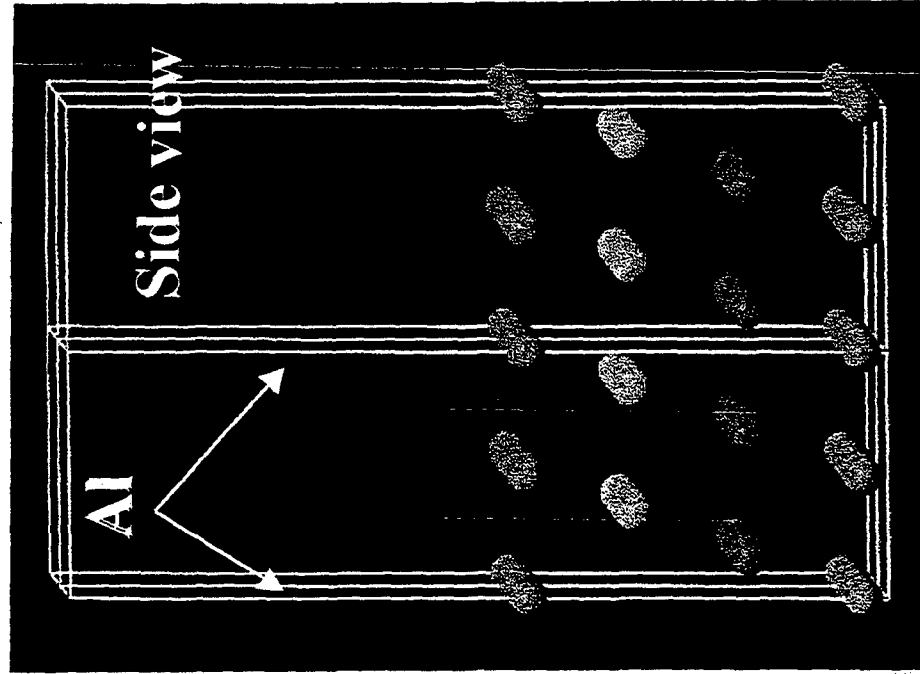
- Two surface models have been used: $(\sqrt{7} \times \sqrt{7})R19.1^\circ$

1. Al(111)-
slab model with 4 layers
(28 Al atoms) for small
molecules (nitromethane)

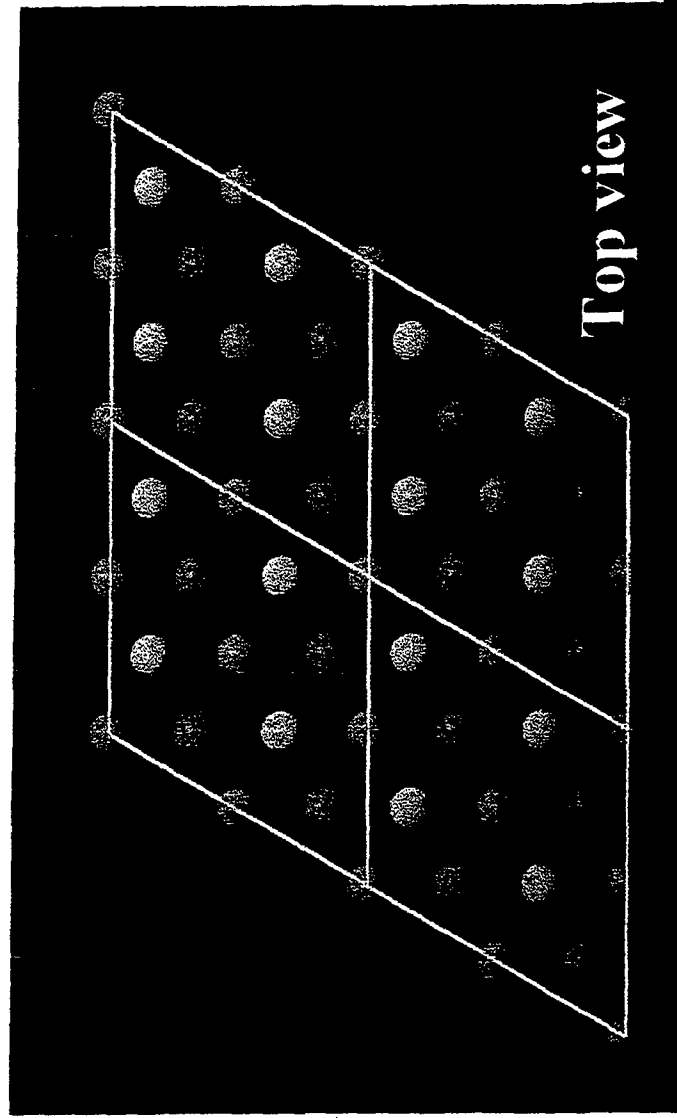


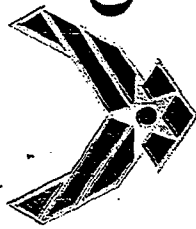


Al(111) Slab Model (II)



2. Al(111)- (3x3) surface units slab model with 4 layers (36 Al atoms) for larger molecules (FOX7, HMX)

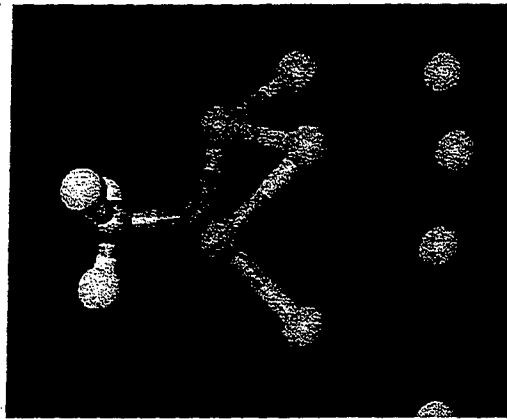




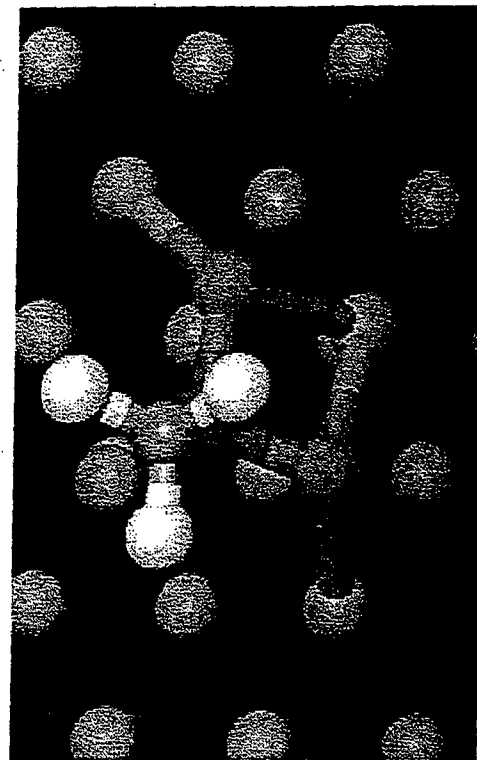
Chemisorption Properties of Nitromethane on Al(111)



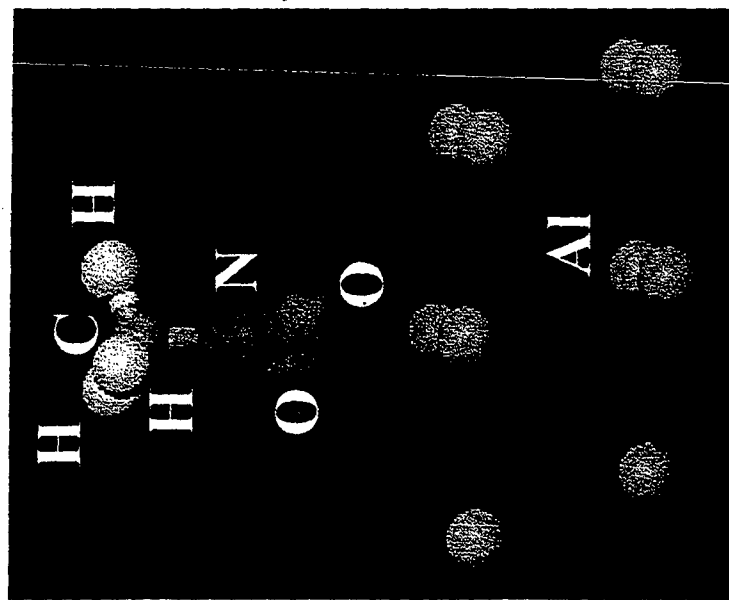
Final configuration



side view



top view



Initial configuration

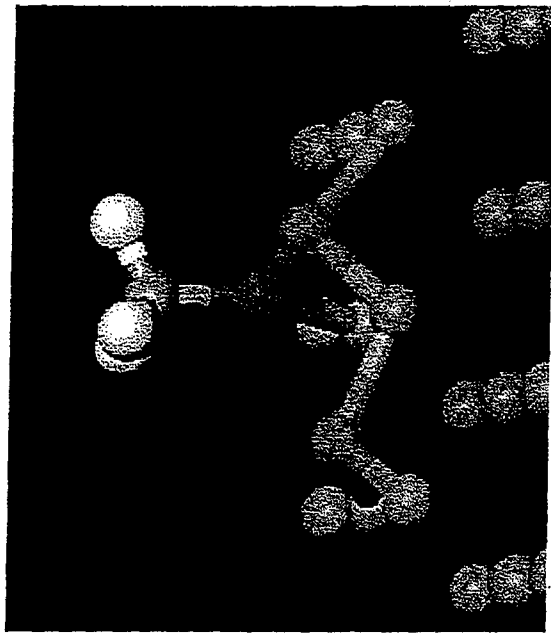
**Formation of strong Al-O bonds;
deformations of NM molecule**



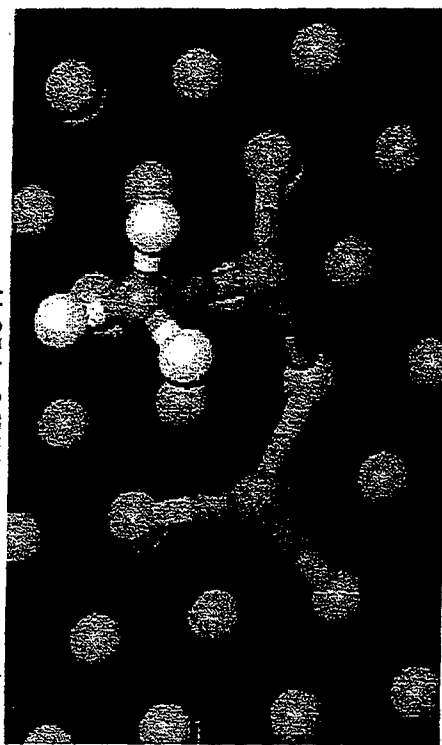
Dissociative Chemisorption of Nitromethane



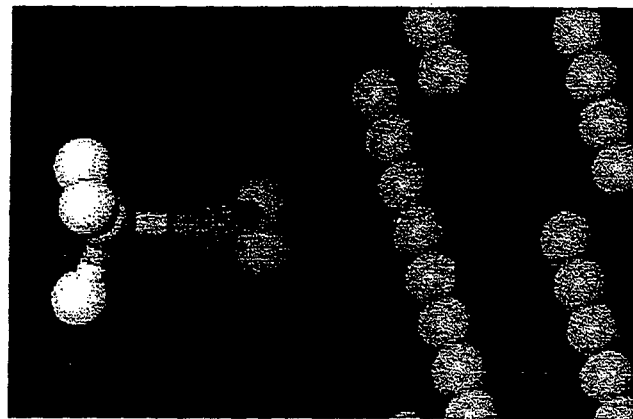
Final configuration



side view



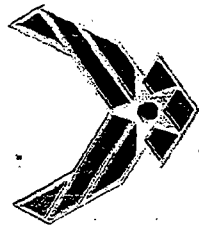
top view



Initial configuration

* Dissociation of NM molecule.

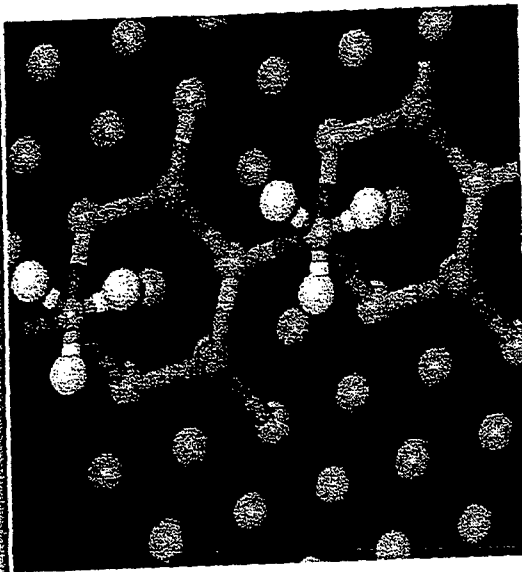
* Oxidation of Al surface atoms.



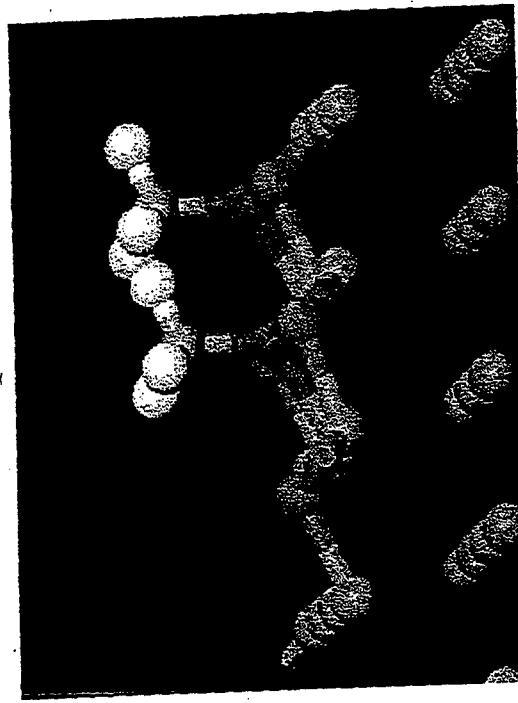
Dissociative Chemisorption of Nitromethane with Complete Elimination of O atoms



Final configuration



top view

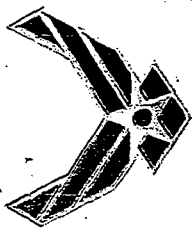


side view

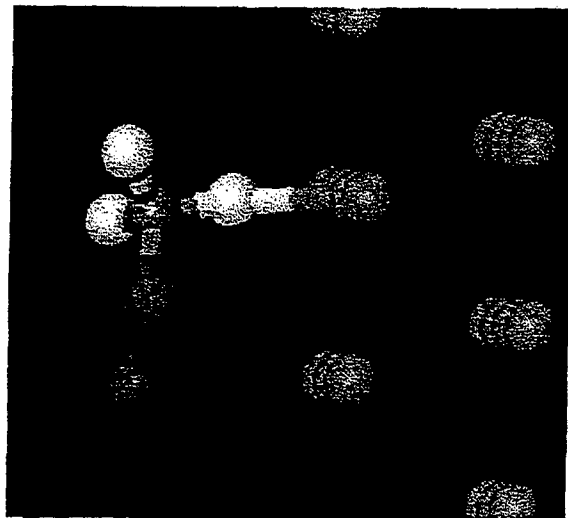
Initial configuration

***Both O atoms are eliminated.**

***Both O atoms contribute to oxidation of Al atoms.**



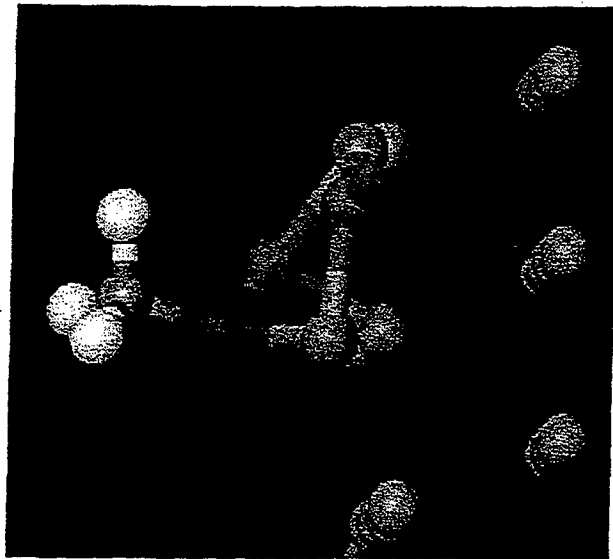
Dissociative Chemisorption of Nitromethane: Molecular Reorientation and N-O Dissociation



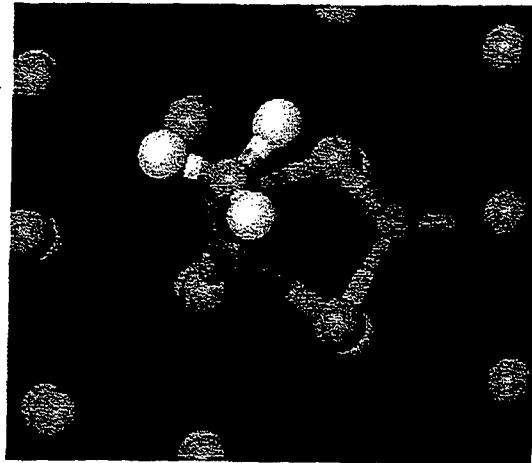
Initial configuration

***rotation of the molecule to maximize Al-O interaction**
***N-O dissociation and formation of Al-O bonds**

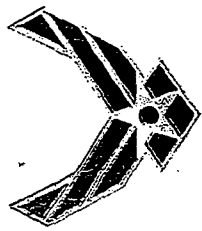
Final configuration



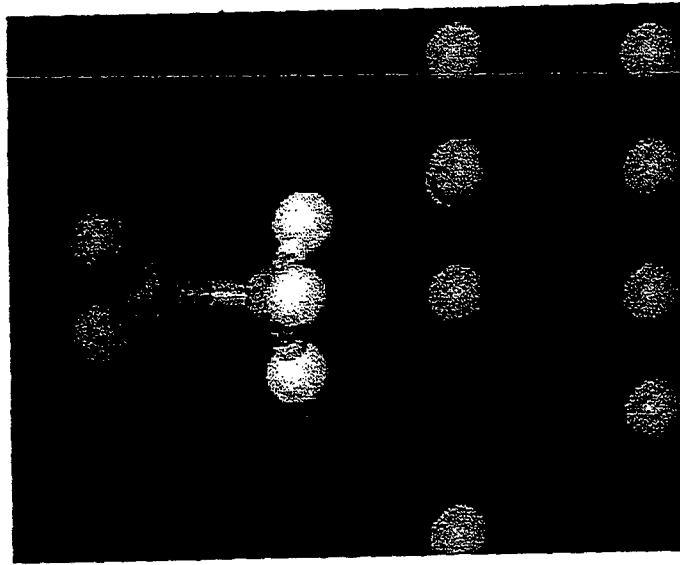
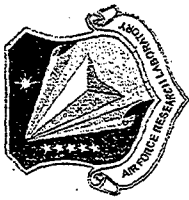
top view



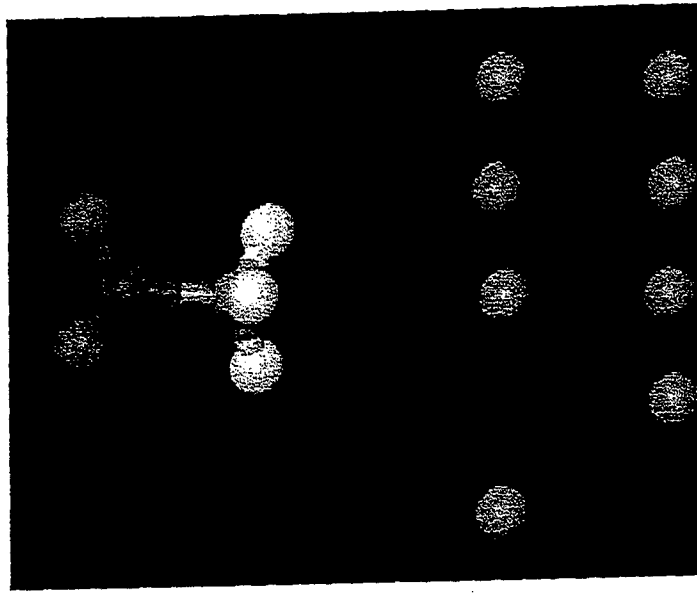
side view



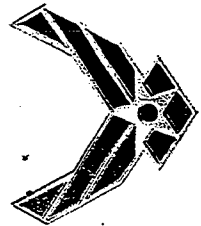
There are configurations in which nitromethane can escape from being adsorbed on the surface.



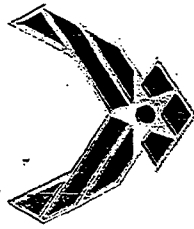
Initial configuration



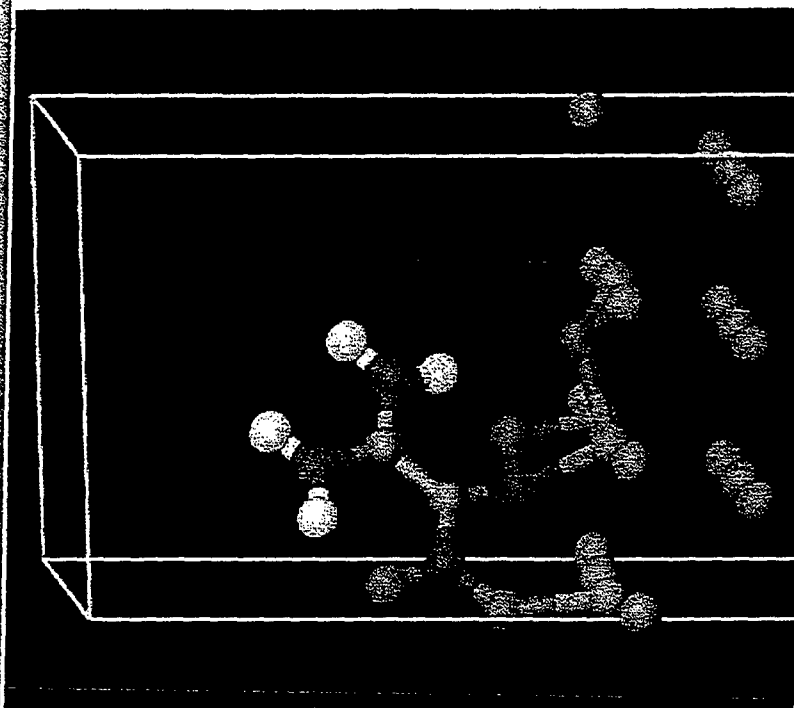
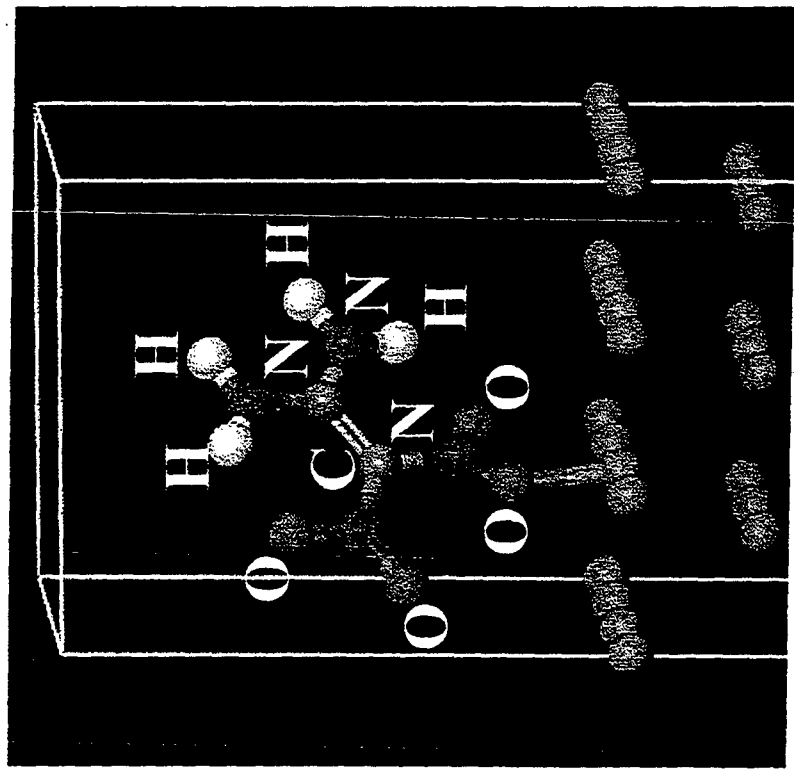
Final configuration



THE AIR FORCE RESERVE COMMISSION



Chemisorption Studies of FOX7 ($C_2N_4O_4H_4$) on Al(111)

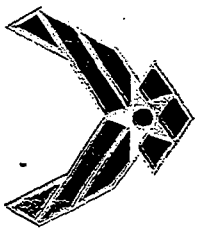


Initial configuration

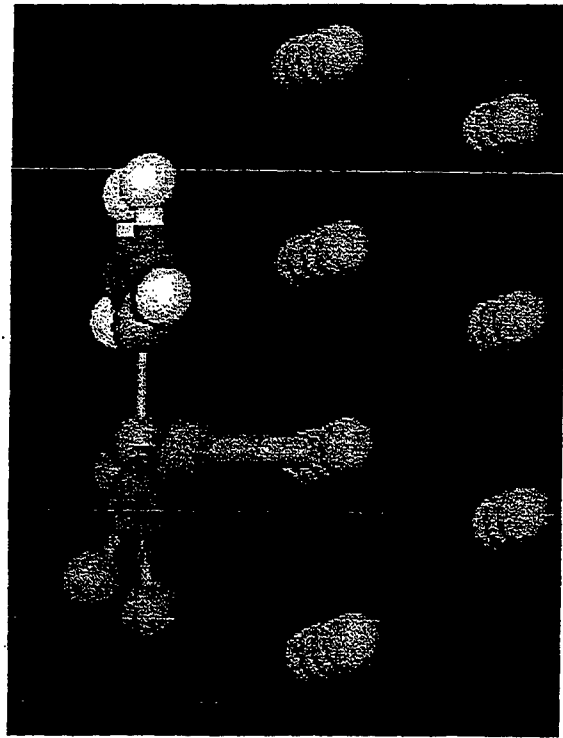
Final configuration

* dissociation of N-O bonds can take place.

* O atom embeds into the lattice

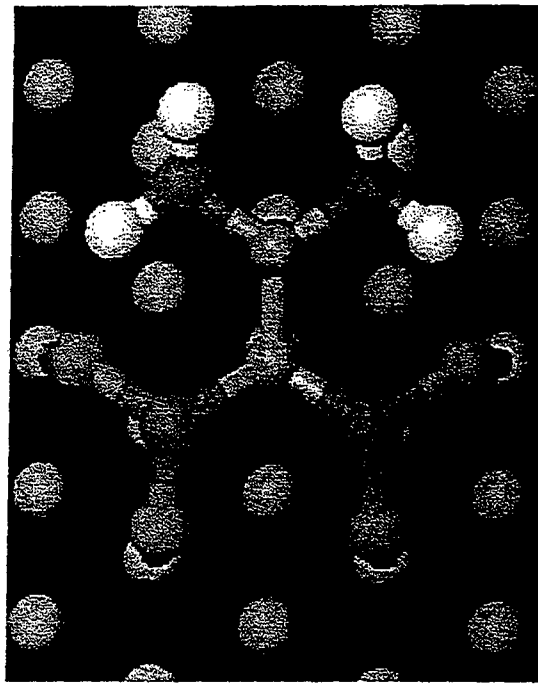
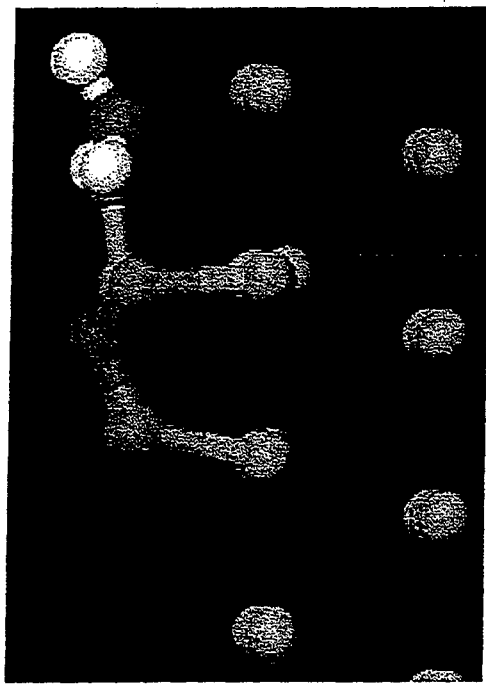


Chemisorption of FOX7 with Formation of Bridged Structures



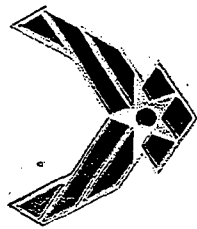
Initial configuration

side view

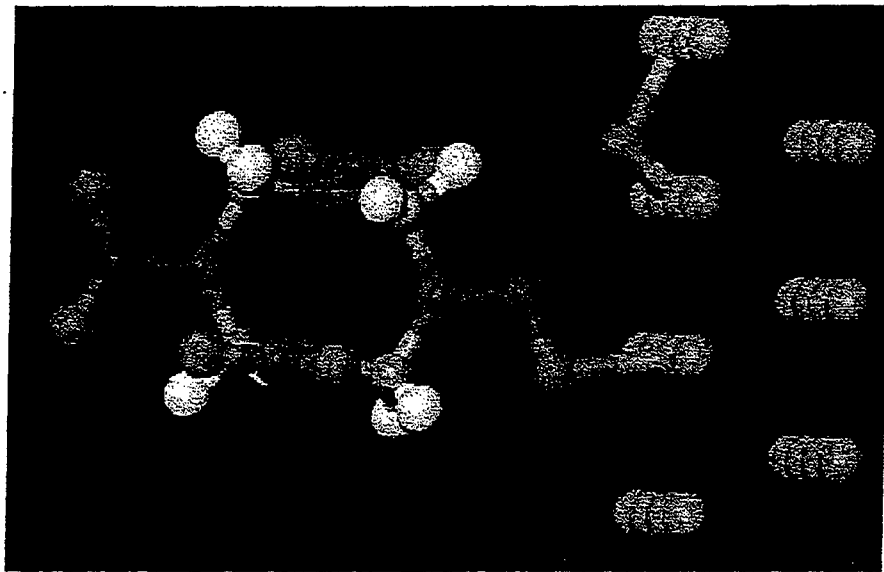


top view

Final configuration 20

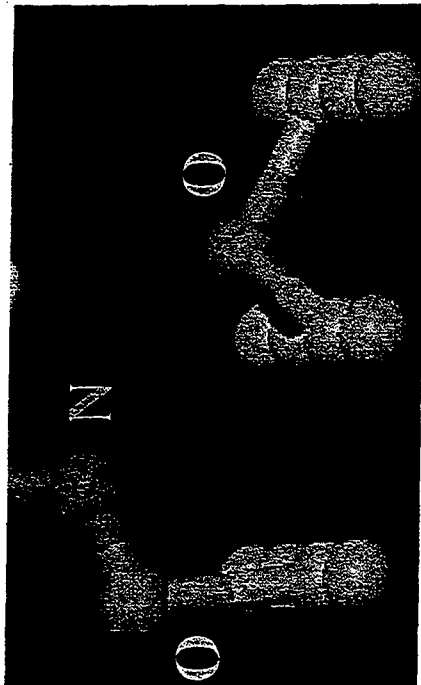
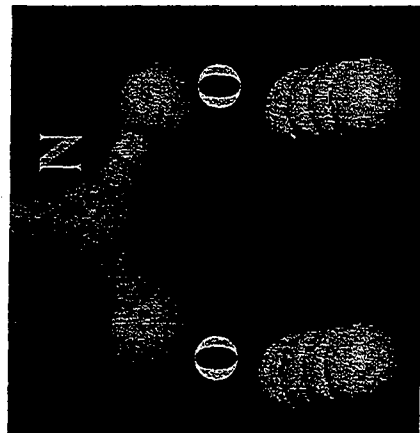
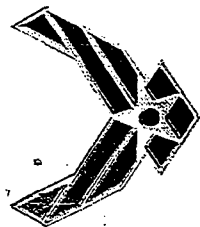


Chemisorption Studies of HMX ($C_4N_8O_8H_8$) on Al(111)

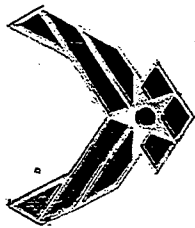


**For HMX we observe a similar process:
dissociation of NO_2 groups with formation of Al-O bonds**

Conclusions



Dissociation of NO_2 (from either C-NO_2 or N-NO_2) with formation of Al-O bonds seem to be a general process in compounds containing nitro groups.

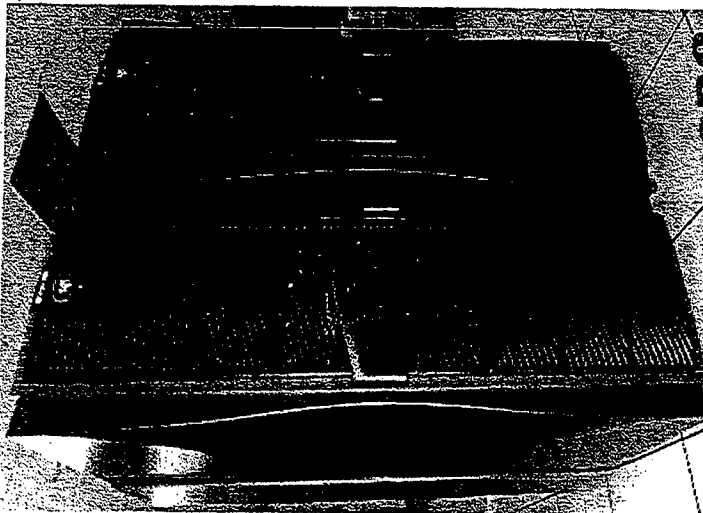


Summary



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

- Dissociation of one or more oxygen atoms, with subsequent chemisorption of the radical fragments on the aluminum surface, is a common mechanism for nitro-containing molecules.
- Nitro-containing molecules will not fully inhibit formation of an oxide layer on the surface of aluminum.



DOD ARL MSRC
NAVO MSRC

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