

# REPORT DOCUMENTATION PAGE

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FILE

MEMORANDUM FOR PRS (Contractor Publication)

FROM: PROI (STINFO)

19 May 2003

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-VG-2003-138

5364 Boatz, Jerry (PRSP), "New Materials Design"

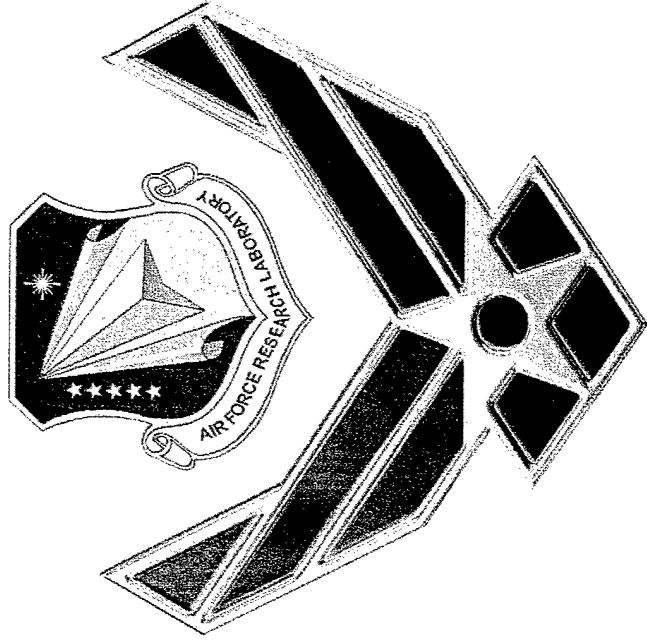
DoD High Performance Computing Users Group Conference  
(Bellevue, WA, 9-13 Jun 2003) (Deadline = 9 Jun 2003)

(Statement A)

# New Materials Design

DoD UGC, 9-13 June 2003

Bellevue, WA

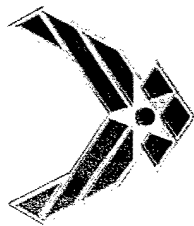


Jerry Boatz

Senior Research Chemist

Propulsion Directorate

Air Force Research Laboratory



# NEW MATERIALS DESIGN



## THE TEAM....

Prof. Mark S. Gordon

Prof. Gregory Voth

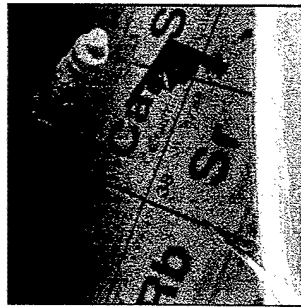


Prof. Sharon Hammes-Schiffer

PENNSYLVANIA

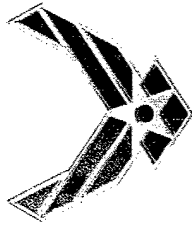


Dr. Ruth Pachter, AFRL/MLPJ



Dr. Jerry Boatz, AFRL/PRSP





# OUTLINE



## 1. Project Overview

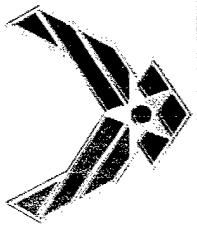
- High energy density materials
- Polyhedral oligomeric silsesquioxanes (POSS)
- Non-linear optical materials

## 2. Theoretical Methods and benchmarks

- Ab initio electronic structure theory
- Nuclear-electronic orbital approach

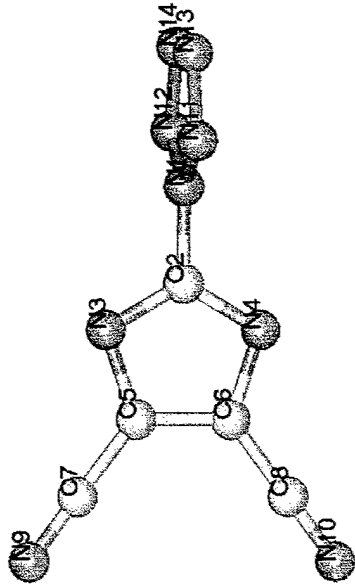
## 3. Results

## 4. Summary

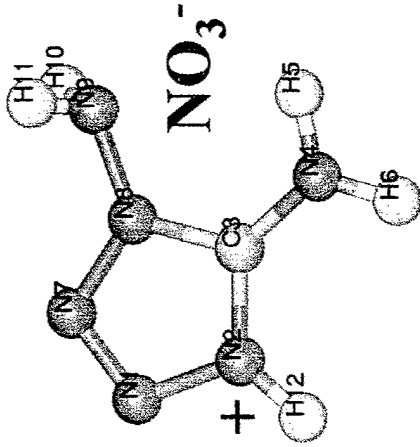


# PROJECT OVERVIEW - HEDM

## High Energy Density Matter -- next generation rocket propellants



High-nitrogen/polynitrogen compounds

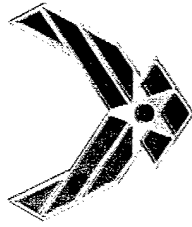


$\text{NO}_3^-$

Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H / m}$$

Energetic Ionic Liquids



# PROJECT OVERVIEW - HEDM



## Technical issues being addressed using CCM

### 1. High-nitrogen/polynitrogen compounds

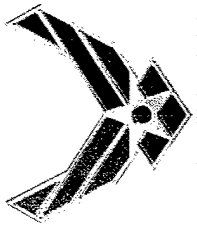
**Objective:** identify, characterize, and synthesize stable compounds with high heats of formation, high densities

- geometries, energy content, stabilities, reaction pathways

### 2. Energetic ionic liquids

**Objective:** identify, characterize, and synthesize thermally stable energetic ILS with low melting points, high densities and low viscosities.

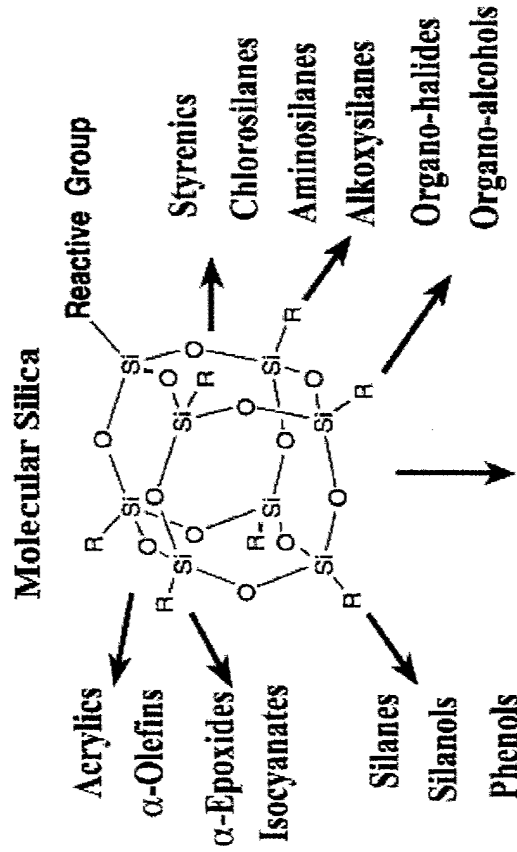
- geometries, electronic structures, stabilities, energy content, interaction potentials



# PROJECT OVERVIEW - POSS



## Polyhedral oligomeric silsesquioxanes -- next generation plastics



### As Additives

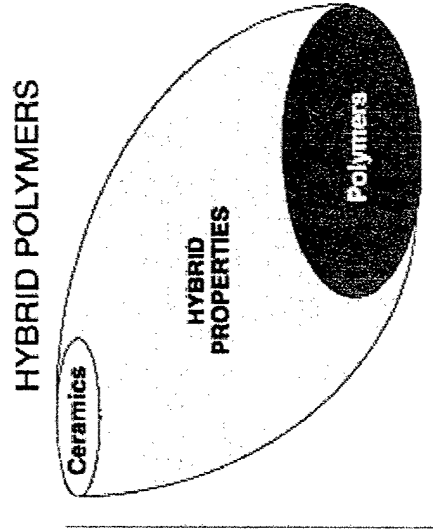
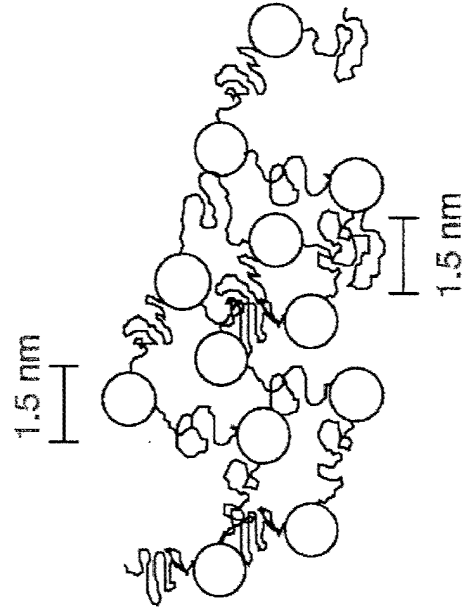
Heat/abrasion resistant paints and coatings  
 Mechanical property/viscosity/thermal modifiers  
 Crosslinking agents  
 Fire retardants

### As Plastics

Medical materials  
 Space resistant resins  
 Packaging/coatings  
 Electronic materials  
 Optical Plastics

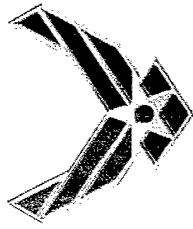
### As Preceramics

Ablative materials (nozzles, insulations etc.)  
 Claddings/electronics coatings  
 Precursors to glassy or ceramic matrices



Use  
 Temperature

Toughness



# PROJECT OVERVIEW - POSS



## Technical issues being addressed using CCM

### 1. Mechanisms of formation

**Objective: rational design and synthesis of POSS**

- role of solvents, acid/base catalysis, substituent effects on mechanism of formation

### 2. Potential applications as molecular “sieves”

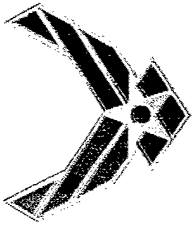
**Objective: determine if POSS cages can be used to separate small molecules**

- determine barriers to encapsulation of  $N_2$  and  $O_2$

### 3. Ti-POSS as new catalysts

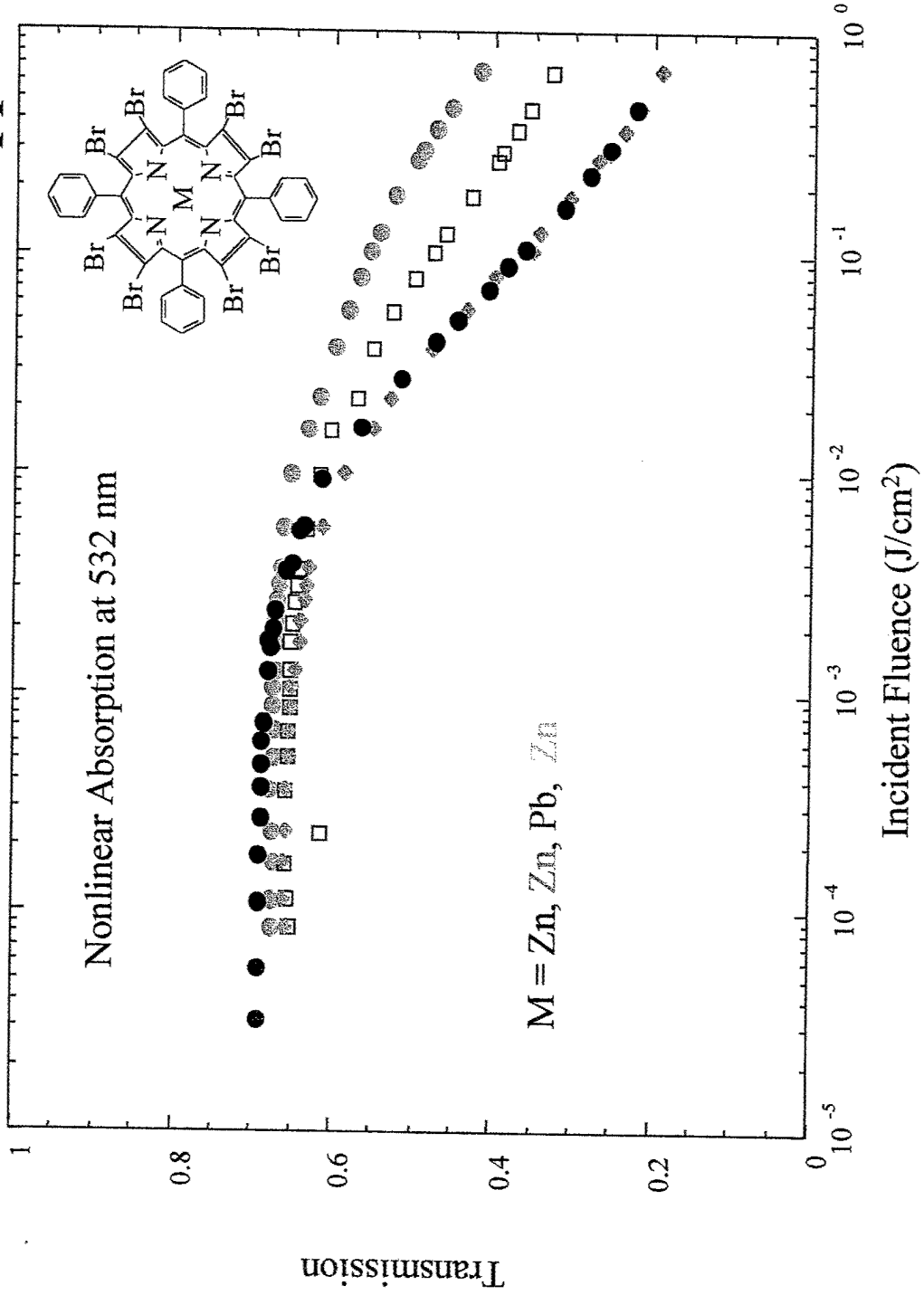
**Objective: determine if Ti-POSS and Ti-siloxane compounds are effective catalysts**

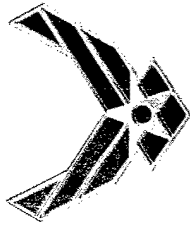
- determine barriers to polymerization of ethylene, oxidation by HOOH.



# PROJECT OVERVIEW - NLO

## Non-linear optical materials for laser-hardened applications



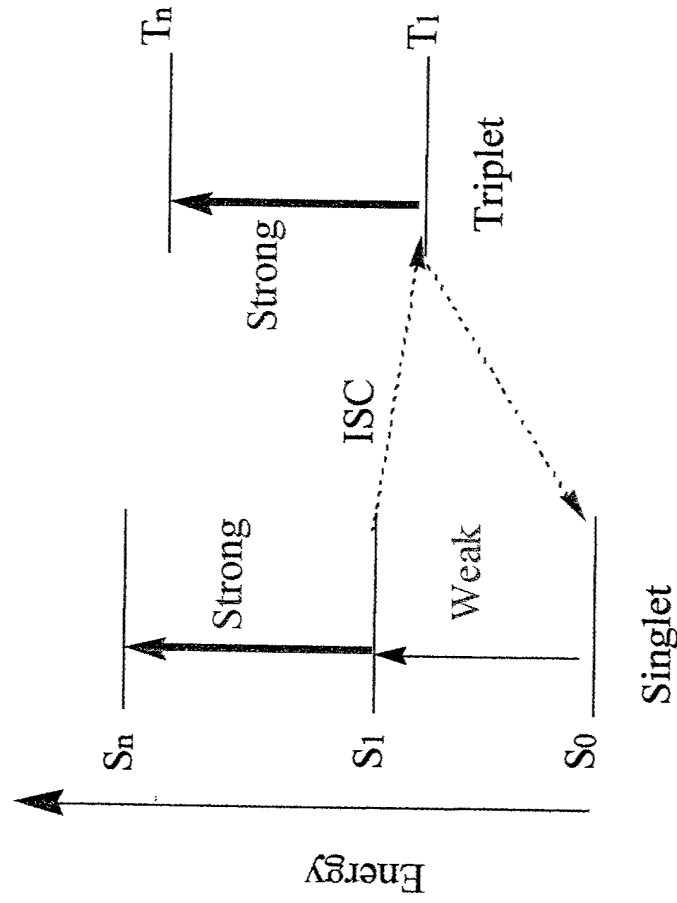


# PROJECT OVERVIEW - NLO



## Technical issues being addressed using CCM

### 1. Mechanism of reverse saturable absorption (RSA)



#### Key Components of RSA

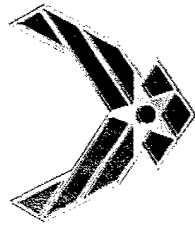
Ground state spectra (linear response)

Singlet-triplet splittings (ISC, phosphorescence)

Ionization potential (photoionization)

Excited triplet spectra (NLA)

Five-level model for nonlinear absorption



# THEORETICAL METHODS



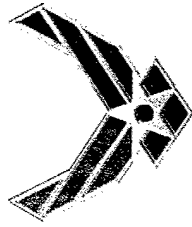
1. Ab initio electronic structure theory
  - General Atomic and Molecular Electronic Structure System (GAMESS) -- a CHSSI code
  - Nuclear-electronic orbital approach (NEO) for including nuclear quantum effects (important, e.g., in proton transfer reactions)

Various computational techniques are employed to solve the molecular electronic Schrödinger equation from quantum mechanics:

$$\left[ -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} \right] \Psi_{el} = E_{el} \Psi_{el}$$

Categories of approximate solutions:

- a) “Self-consistent field” (SCF): reasonably good geometries
- b) “Electron correlation”: post-SCF correction, required for reliable energetics (e.g., barriers).



# THEORETICAL METHODS

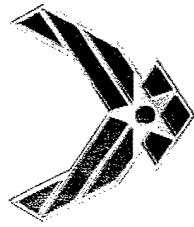


1. Ab initio electronic structure theory (cont.)
  - Most electronic structure codes use Born-Oppenheimer (i.e., “clamped nuclei”) approximation -- NOE method treats specified nuclei at QM level.

## Nuclear-Electronic Hamiltonian

$$\begin{aligned}
 H_{\text{tot}}(\mathbf{r}_e, \mathbf{r}_q; \mathbf{r}_c) = & - \sum_i^{N_e} \frac{1}{2} \nabla_i^2 - \sum_A^{N_e N_c} \frac{Z_A}{r_{iA}} + \sum_i^{N_e N_e} \frac{1}{r_{ij}} \\
 & - \sum_I^{N_p} \frac{1}{2M_I} \nabla_I^2 + \sum_A^{N_p N_c} \frac{Z_A Z_I}{r_{IA}} + \sum_I^{N_p} \sum_{J>I}^{N_p} \frac{Z_I Z_J}{r_{IJ}} \\
 & - \sum_i^{N_e} \sum_I^{N_p} \frac{Z_I}{r_{iI}} + \sum_{A B>A}^{N_c} \frac{Z_A Z_B}{r_{AB}}
 \end{aligned}$$

- $N_e$ : number of electrons (coordinates  $\mathbf{r}_e$ )
- $N_p$ : number of quantum nuclei (coordinates  $\mathbf{r}_p$ )
- $N_c$ : number of classical nuclei (coordinates  $\mathbf{r}_c$ )



# THEORETICAL METHODS



## Ab initio electronic structure theory

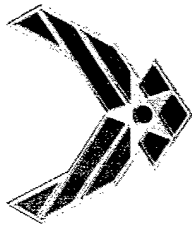
### Current Status of parallel GAMESS

	<u>RHF</u>	<u>ROHF</u>	<u>UHF</u>	<u>GVB</u>	<u>MCSCF</u>
Energy	cdp	cdp	cdp	cdp	cdp
Analytic Gradient	cdp	cdp	cdp	cdp	cdp
Numeric Hessian	cdp	cdp	cdp	cdp	cdp
Analytic Hessian	cdp	cdp	-	cdp	-
MP2 energy	cdp	cdp	cdp	-	c p
MP2 gradient	cdp	-	cd	-	-
CI energy	cdp	cdp	-	cdp	cdp
CI gradient	cd	-	-	-	-
DFT energy	cdp	cdp	cdp	-	-
DFT gradient	cdp	cdp	cdp	-	-

c = conventional disk storage of AO integrals

d = direct evaluation of AO integrals

p = runs in parallel



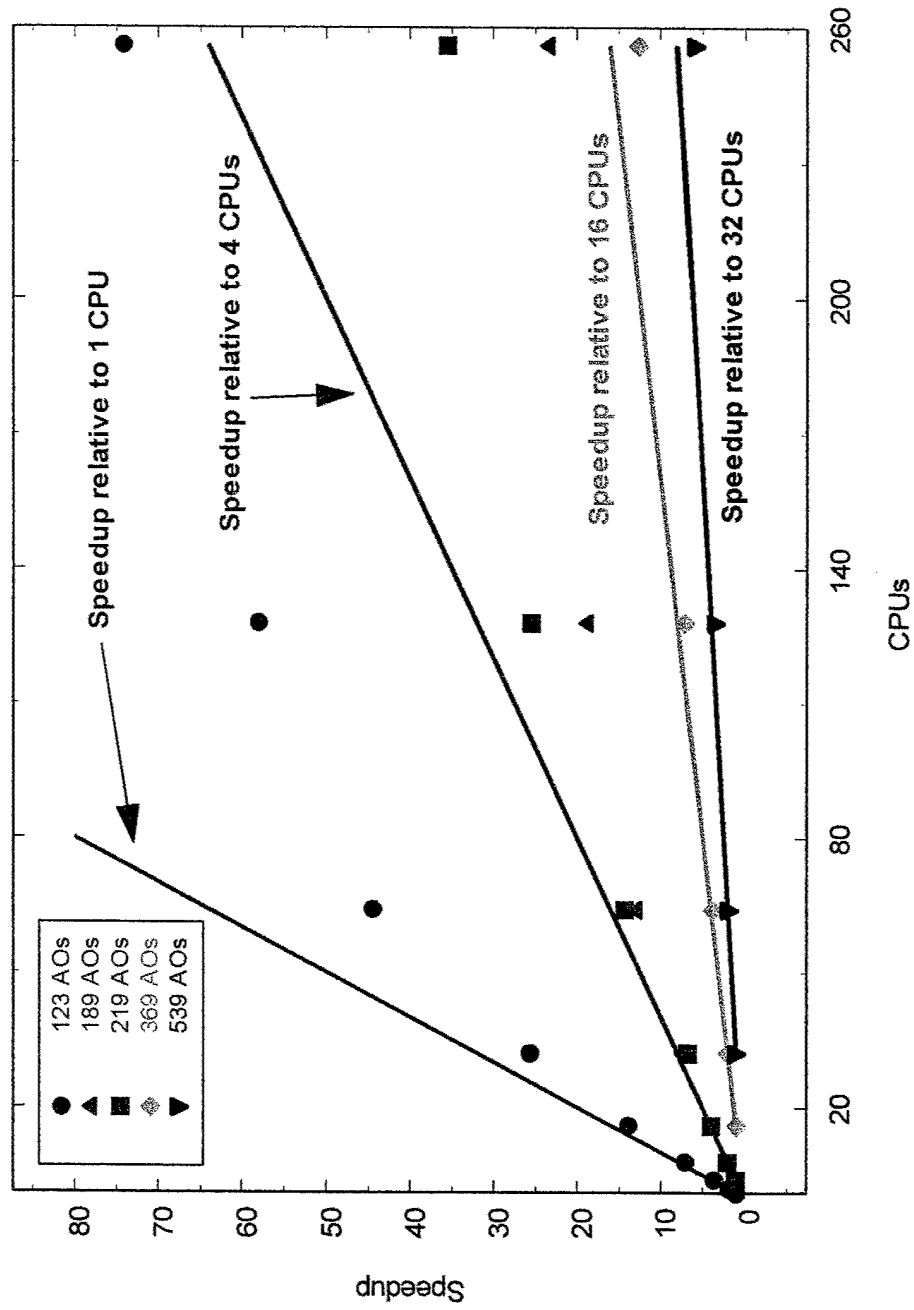
# THEORETICAL METHODS

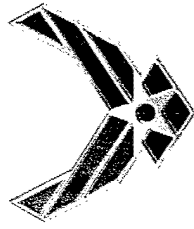


## Ab initio electronic structure theory

### MP2 Gradient Scalability Test

Silicocene molecule,  $\text{Si}(\text{C}_5\text{H}_5)_2$

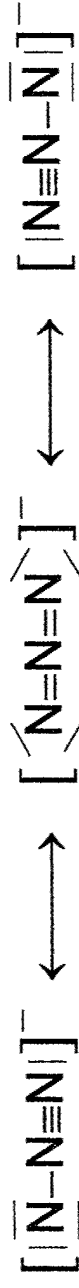




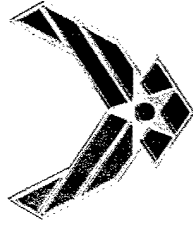
# The Search for New Polynitrogens



- All polynitrogens are unstable with respect to  $N_2$  molecules
- Their activation energy for  $N_2$  elimination is largely determined by the weakest bond in the compound
- Their metastability is enhanced if suitable resonance structures exist:



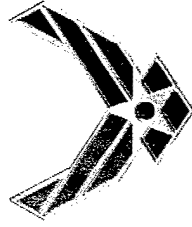
- The double-bond character of the  $\text{N}-\text{N}$  bonds in the azide anion explains its exceptional stability
- How can this stabilization effect be used to our advantage in preparing new compounds?



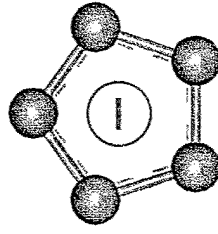
# Pentazolates ( $N_5^-$ )?



- Substituted pentazoles  $R-N_5$  have been known for decades ( $R=aryl$ )
- Cyclic  $N_5^-$  is aromatic
- Conversion of the diazonium salt,  $RN_2^+$ , to the substituted pentazole ring  $R-N_5$  by the reaction with azide ion,  $N_3^-$ , has been demonstrated many years ago by Ugi and Huisgen.
- $N_5^-$  has been recently detected in the gas phase for the first time, using collisional fragmentation (electrospray ion mass spectroscopy).
- Can a chemical route to  $N_5^-$  be found? (e.g., can a suitable R group be found for the reaction  $R-N_2^+ + N_3^- \rightarrow R-N_5 \rightarrow R^+ + N_5^-$ ?)

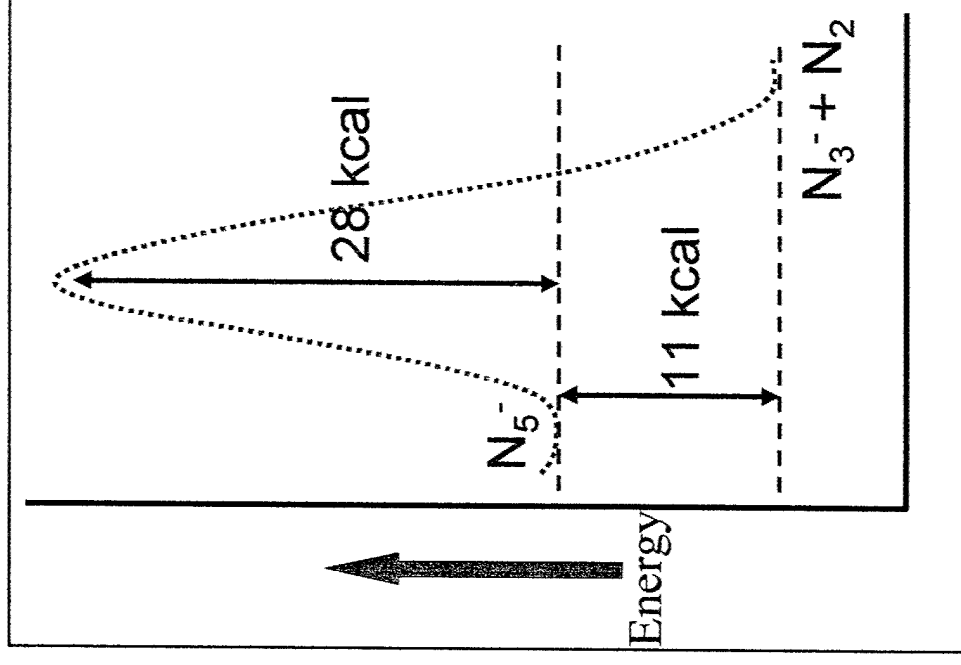


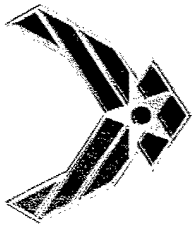
# New Polynitrogen Anions



## Pentazole anion ( $N_5^-$ )

- Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to  $N_3^-$  and  $N_2$  is only 11 kcal/mol exothermic
- Aryl substituted pentazoles can be isolated as stable compounds only if stored at low temperatures. In methanol, these compounds rapidly decompose at room temperature to form aryl azides and  $N_2$  gas



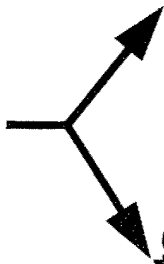


# Synthetic Challenge – How do we make These New Anions??

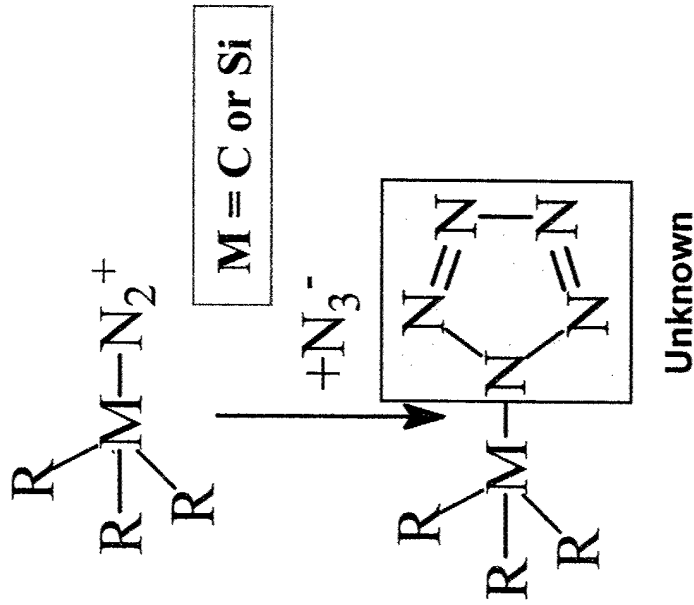


## Synthesis of Substituted Pentazoles

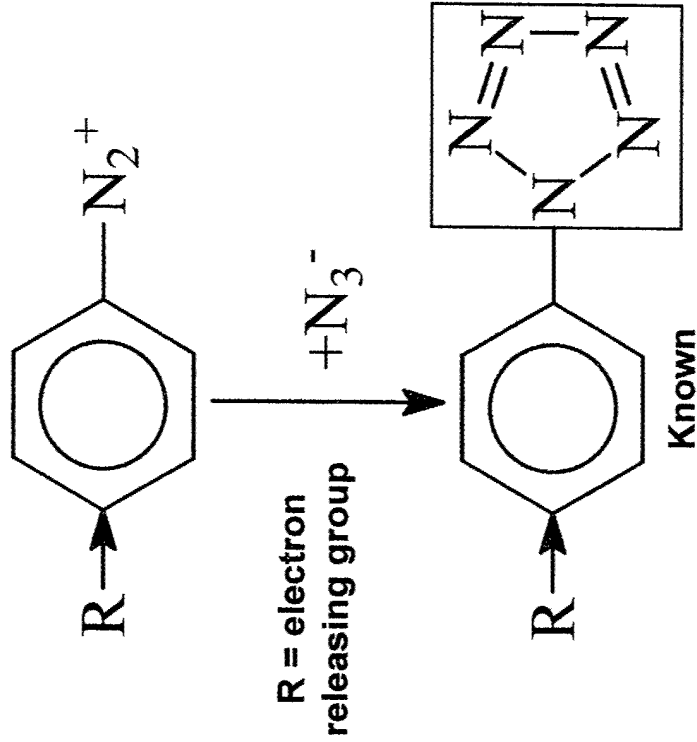
### Sources for the Pentazole Anion ( $N_5^-$ )

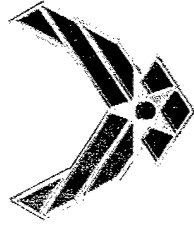


Trityl/Silyl Diazonium Salts



Aryl Diazonium Salts





# Theoretical Challenge - Can we design and predict viable precursors to $N_5^-$ ?



Find a substituent R so that

1.  $R-N_2^+$  is stable wrt  $R^+ + N_2$ .
2. The R-N bond in  $R-N_5$  is weak, thereby suitable for the reaction  $R-N_5 + M^+X^- \rightarrow M^+N_5^- + R-X$

## Approach

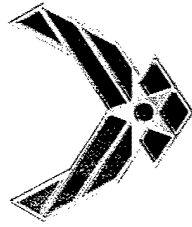
Use quantum chemical calculations to predict the stability of  $R-N_2^+$  diazonium salts and the length/strength of the  $R-N_5$  bond.

MBPT(2)/6-31G(d) level of theory

M = C, Si

$L_3M-N_2^+$

L = F, Cl,  $CH_3$ ,  $CF_3$ ,  $NO_2$ , phenyl, etc.

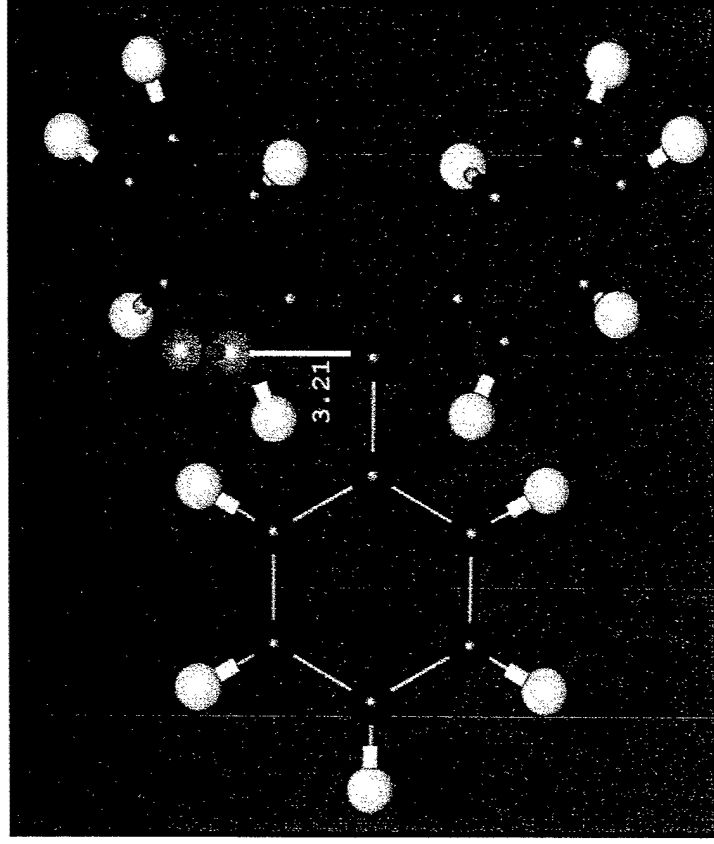
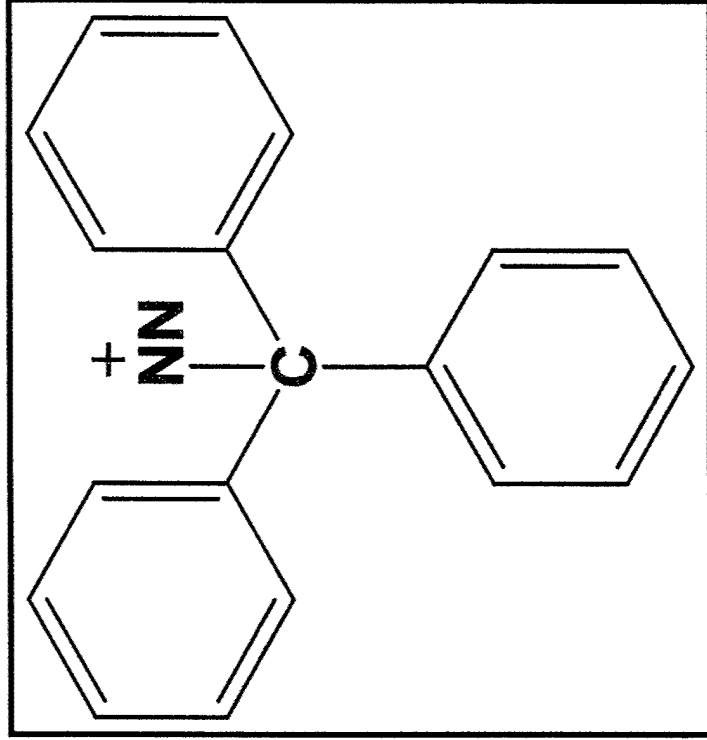


## Identifying Precursors for New Polynitrogens

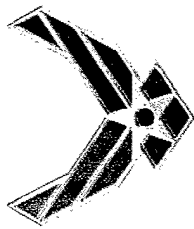


*This ion has been suggested as a useful precursor to new polynitrogen molecules...*

*... but calculations predict it to be unstable.*



Computational requirements: ~50,000 CPU-hours, 1.2 GW on IBM SP/P3 at ASC

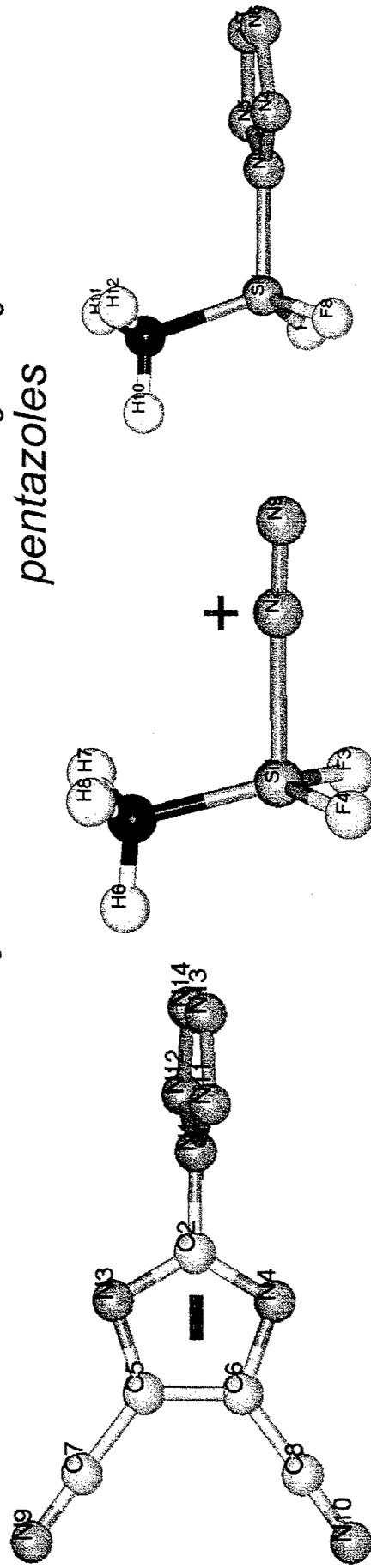


# RESULTS - HEDM



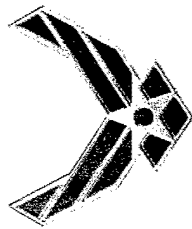
## High-nitrogen/polynitrogen compounds

Potential dicyanoimidazolate precursor to displacement of  $N_5^-$  formation of suitable  $R_3Si-N_5$  substituted pentazoles



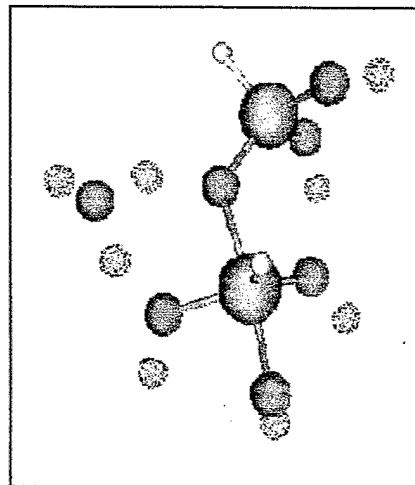
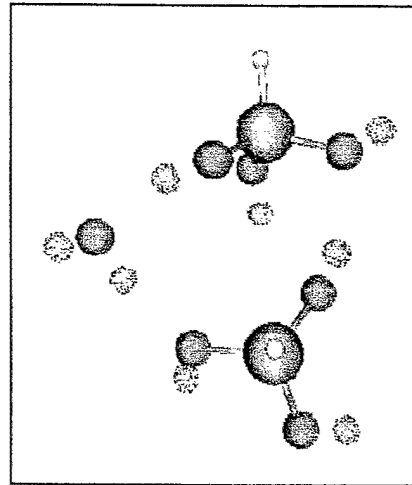
$R_3$	$R_3Si-N_2^+$ distance(A)	$D_e(Si-N_2^+)$ (kcal/mol)	$R_3Si-N_5$ distance (Å)
3Me	2.151	13.8	1.855
2Me,F	2.144	15.7	1.834
Me,2F	2.151	21.2	1.855
3F	1.973	33.4	1.783

Computational requirements: ~50,000 CPU-hours, 1 GW on IBM SP/P3 at ASC

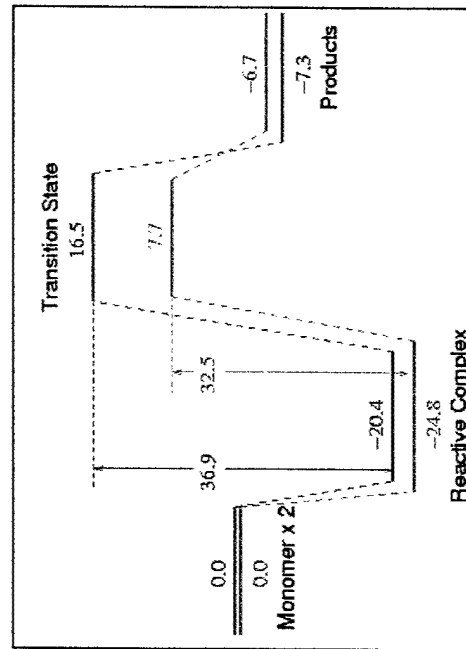
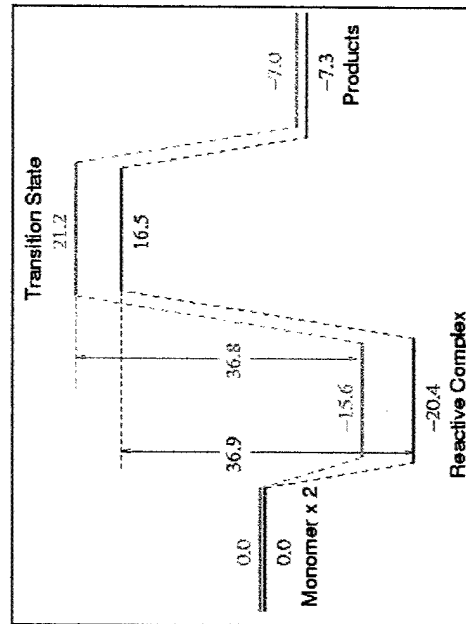


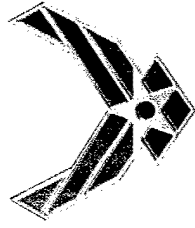
# RESULTS - POSS

Nuclear quantum effects in water-catalyzed condensation reactions



Level	Reactive		Transition State	Products	CPU Time
	Complex	Complex			
RHF/6-31G*	-20.4	16.5	16.5	-7.3	1.0
RHF/6-31G*/ZPE	-15.6	21.2	21.2	-7.0	1.1
NEO/HF/4	-23.0	7.2	7.2	-5.9	1.1
NEO/HF/8	-24.8	7.7	7.7	-6.7	1.8





## POSS as catalysts?

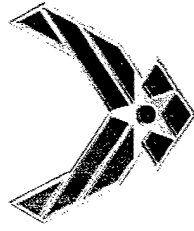


Some Ti compounds are known to be effective catalysts

Ziegler-Natta, olefin oxidation

Recent experiments reveal Ti-modified silicates catalyze olefin oxidation by peroxides

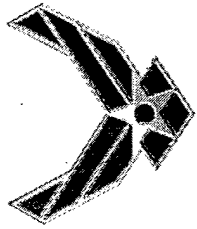
Can Ti-substituted siloxanes and/or POSS catalyze olefin oxidation by HOOH, or polymerization?



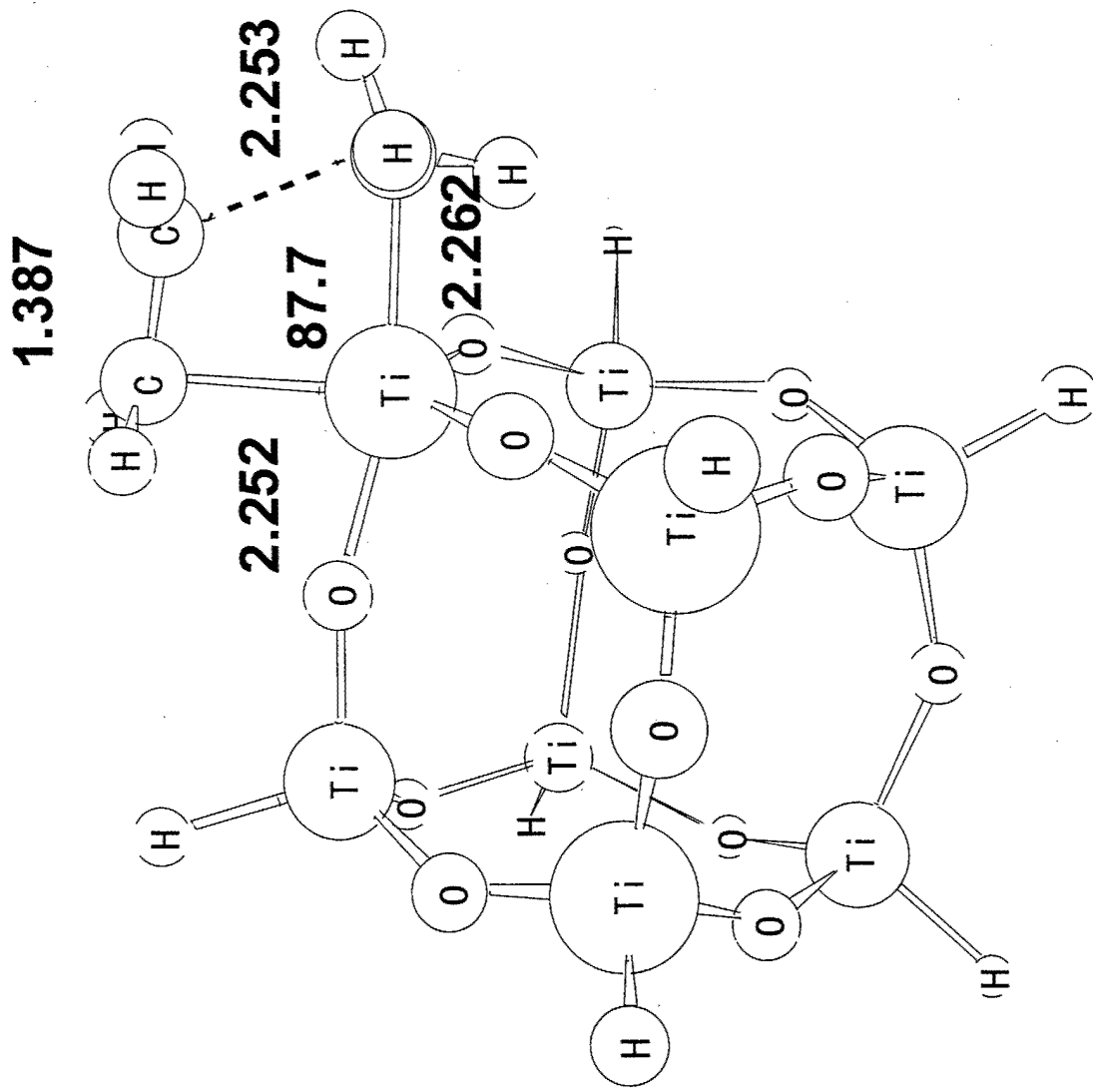
## POSS computational methods



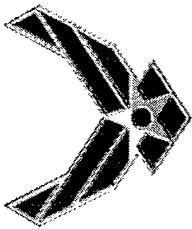
- § B3LYP/6-31G(d) geometry optimizations
- § Hessians to characterize stationary points
- § Energies using MP2/TZVP
- § Some geometries re-optimized with MP2
- § Size of basis set: ~1,000 basis functions
- § Calculations performed at ERDC (T3E) and AHPARC (T3E)



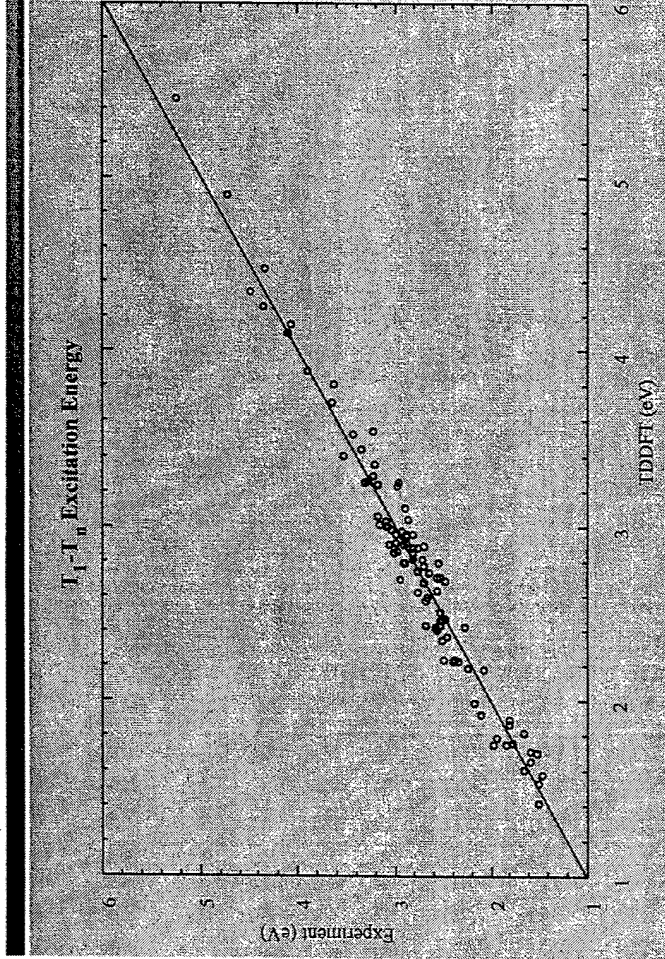
# TS For Polymerization of Ethylene





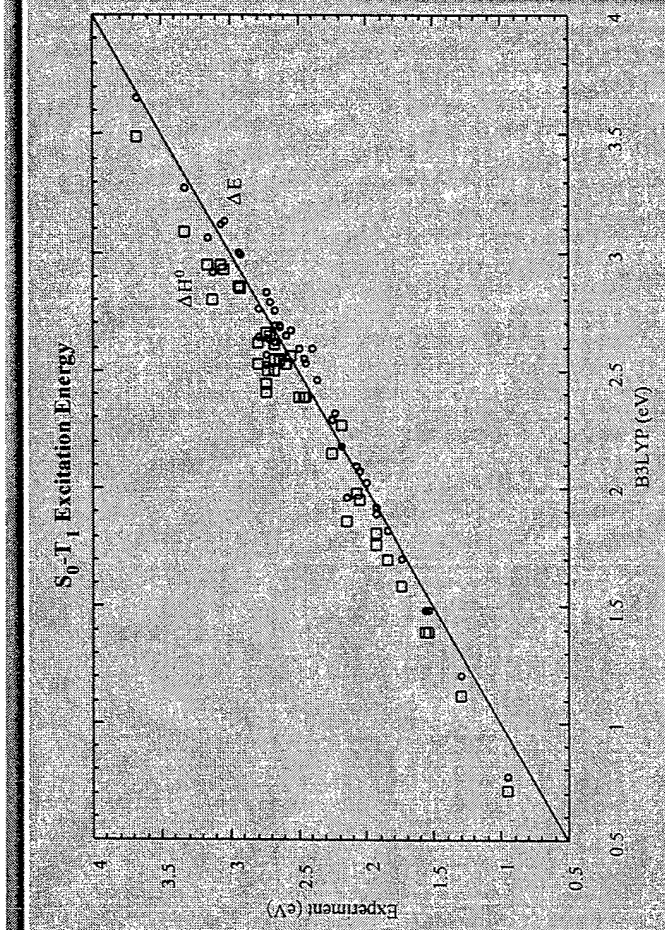


# RESULTS - NLO



**Computed T<sub>1</sub>-T<sub>n</sub> compared to experimental results**

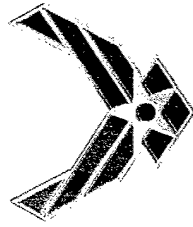
**86 Experimental Values (in solution)**  
**Mean Absolute Error = 0.11**  
**Maximum Error = 0.31**



**Computed S<sub>0</sub>-T<sub>1</sub> compared to experimental results**

**47 Experimental Values (in solution)**  
**Mean Absolute Error = 0.14**  
**Maximum Error = 0.33**

**100,000 hours on SGI O2K, Compaq GS320, IBM SP/P3 at ASC**



# SUMMARY

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## High Energy Density Matter

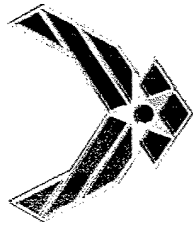
- High-nitrogen/polynitrogen compounds are substantially more energetic than hydrazine.
- Trityldiazonium cation is not a stable polynitrogen precursor.
- Trimethylsilyldiazonium cation is marginally stable, replacement of methyls with fluorines increases stability.

## Polyhedral Oligomeric Silsesquioxanes (POSS)

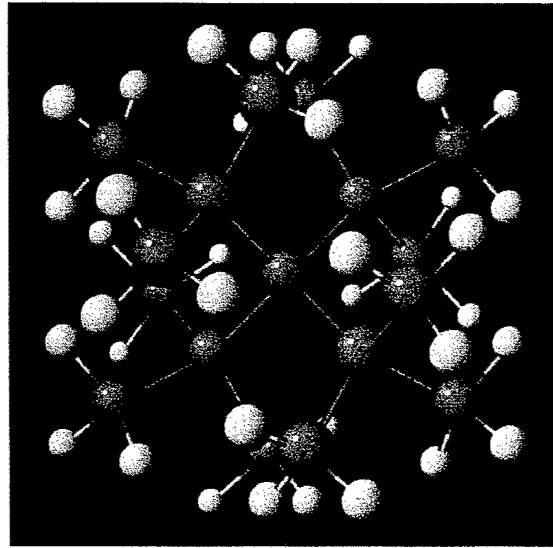
- Nuclear quantum effects are important in proton transfer reactions -- lower barriers by about 4 kcal/mol for water-assisted condensation of trisilanol
- Most effective catalyst for olefin polymerization is  $T_4$  cage
- Barrier is still ~10 kcal/mol too high: Ti-POSS, Ti-siloxanes may not be good catalysts for this reaction

## NLO materials

- Time-dependent density functional theory accurately predicts NLA in free-base porphyrins, phthalocyanines, and their metal complexes.
- Mean absolute error of 0.11 eV for computed triplet-triplet excitation energies
- Mean absolute error of 0.14 eV for computed singlet-triplet excitation energies

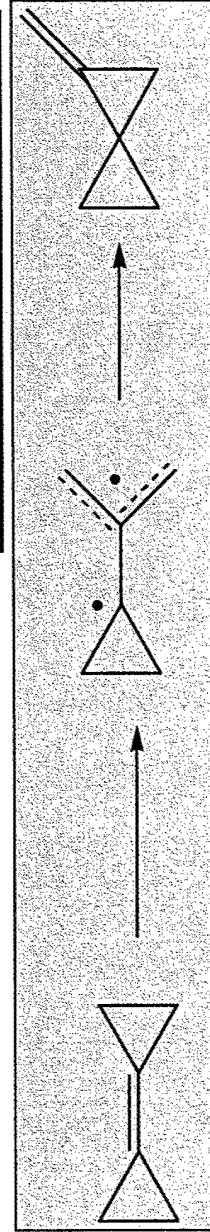


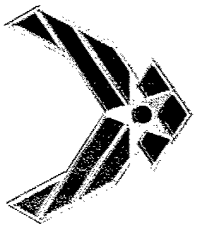
# FUTURE DIRECTIONS



## HEDM

- Thermal decomposition mechanisms of energetic hydrocarbons (e.g., BCP).
- Energetic Ionic Liquids (QSPR models)





# ACKNOWLEDGEMENTS



**POSS:** Takako Kudo, Shawn Phillips, Simon Webb, Frank Feher, Joe Lichtenhan

**HEDM:** Jeff Mills, Greg Drake, Karl Christe, Bill Wilson, Ashwani Vij, Vandana Vij

**NLO:** Kiet Nguyen, Paul Day

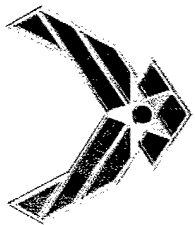
**GAMESS:** Graham Fletcher

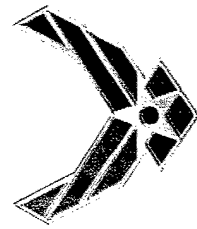
**MSRCs, DCs:** ASC, ARL, ERDC, NAVO, MHPCC, AHPCC, ARSC, AFFTC

**CHSSI funding (CCM-2, CCM-4, MBD-01)**



# Backup Slides





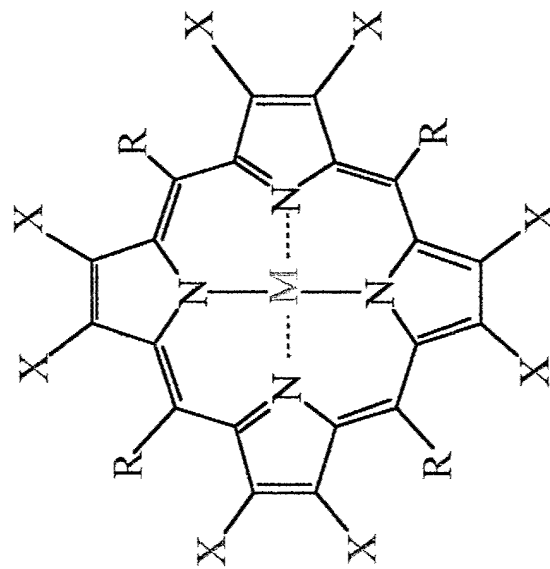
# PROJECT OVERVIEW - NLO



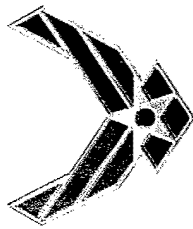
## Technical issues being addressed using CCM

### 2. "Tuning" of absorption spectrum by benzannulation, halide substitution

System	M	X	R	IP	S <sub>0</sub> -S <sub>n</sub>	S <sub>0</sub> -T <sub>1</sub>	T <sub>1</sub> -T <sub>n</sub>
PH <sub>2</sub>	H <sub>2</sub>	H	H	E, C	E, C	E, C	E, C
ZnP	Zn	H	H	E, C	E, C	E, C	E, C
TPPH <sub>2</sub>	Zn	H	φ	E, C	E, C	E, C	E, C
ZnTPP	Zn	H	φ	E, C	E, C	E, C	E, C
ZnTPPBr <sub>8</sub>	Zn	Br	φ	C	E, C	E, C	E, C



IP = Ionization Potential, S<sub>0</sub>-S<sub>n</sub> = Ground State Spectrum,  
S<sub>0</sub>-T<sub>1</sub> = Singlet-Triplet Gap T<sub>1</sub>-T<sub>n</sub> = Triplet-Triplet Spectrum  
E = Experiment, C = Calculated



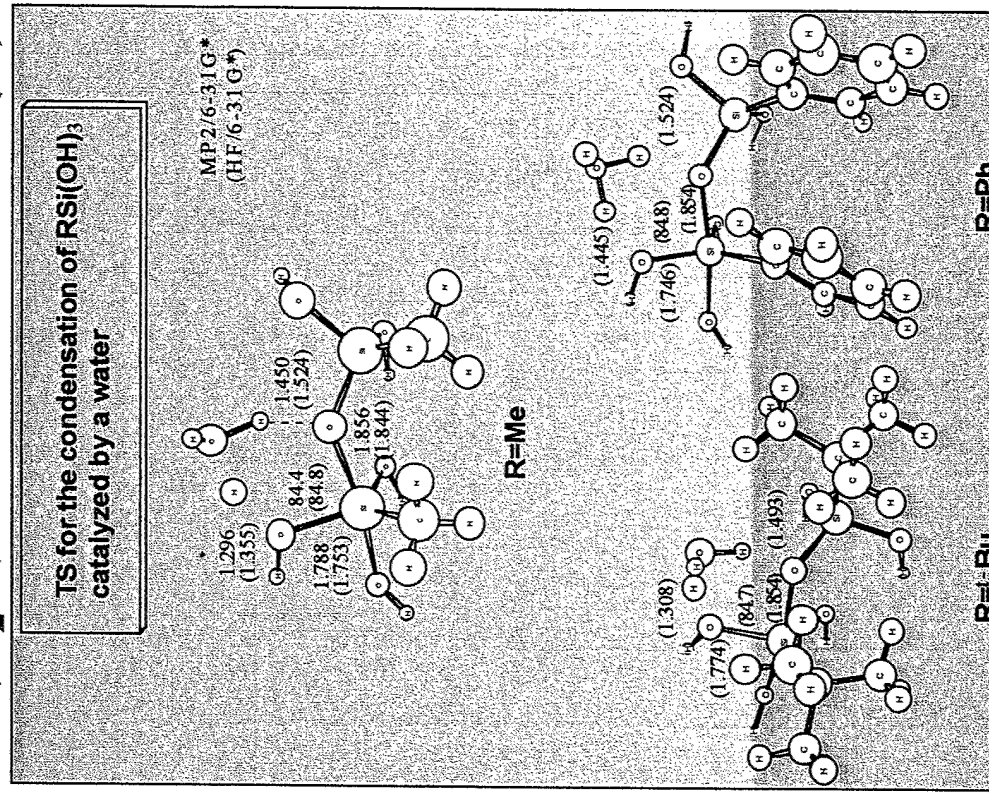
# RESULTS - POSS



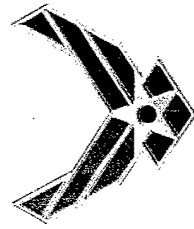
## Mechanism of formation: role of solvent ( $H_2O$ ) & substituents (R)

R	Energy barrier (kcal/mol)	MP2/6-31G*
H	30.4 (16.7)	10.9 (-9.3)
Me	28.2 (14.7)	7.7 (-13.3)
t-Bu	34.3 (24.9)	9.8 (-9.3)
Ph	31.1 (18.2)	7.9 (-16.4)

Values in parentheses are for water-catalyzed results.



Kudo, T., Gordon, M.S. J. Am. Chem. Soc., 120, 11432 (1998)  
 Kudo, T., Gordon, M.S. J. Phys. Chem. A, 104, 4058 (2000)



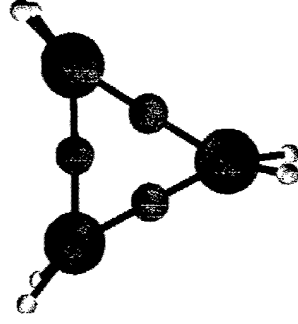
# RESULTS - POSS



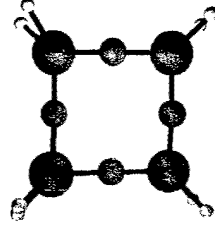
## Mechanism of formation

### Key steps

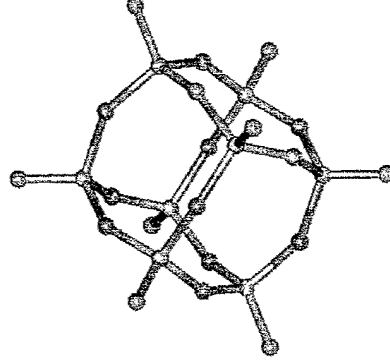
1. Hydrolysis of  $\text{RSiX}_3$  ( $\text{R}=\text{H}, \text{CH}_3, \text{t-butyl}$ , etc.;  $\text{X}=\text{Cl}$ )  
 $\text{RSiCl}_3 + \text{H}_2\text{O} \rightarrow \text{RSiCl}_2\text{OH} + \text{HCl}$   
 $\text{RSiCl}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{RSiCl(OH)}_2 + \text{HCl}$   
 $\text{RSiCl(OH)}_2 + \text{H}_2\text{O} \rightarrow \text{RSi(OH)}_3$
2. Condensation of  $\text{RSi(OH)}_3$  to disiloxane  
 $2 \text{RSi(OH)}_3 \rightarrow \text{R(OH)}_2\text{SiOSi(OH)}_2\text{R} + \text{H}_2\text{O}$
3. Condensation of disiloxane to  $\text{D}_3, \text{D}_4$   
 $\text{RSi(OH)}_3 + \text{R(OH)}_2\text{SiOSi(OH)}_2\text{R} \rightarrow \text{D}_3 + 2\text{H}_2\text{O}$   
 $[2+2]: 2\text{R(OH)}_2\text{SiOSi(OH)}_2\text{R} \rightarrow \text{D}_4 + 2\text{H}_2\text{O}$   
 $[3+1]: \text{RSi(OH)}_3 + \text{R(OH)}_2\text{SiOSi(OH)}_2\text{R} \rightarrow \text{D}_4 + 2\text{H}_2\text{O}$   
Ring Expansion:  $\text{RSi(OH)}_3 + \text{D}_3 \rightarrow \text{D}_4 + \text{H}_2\text{O}$
4. Condensation of  $\text{D}_3, \text{D}_4$  to POSS (in progress)  
 $2\text{D}_4 \rightarrow \text{T}_8 + 4\text{H}_2\text{O}$   
....



D3

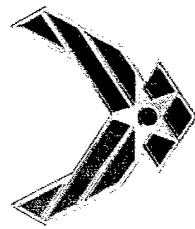


D4



T8

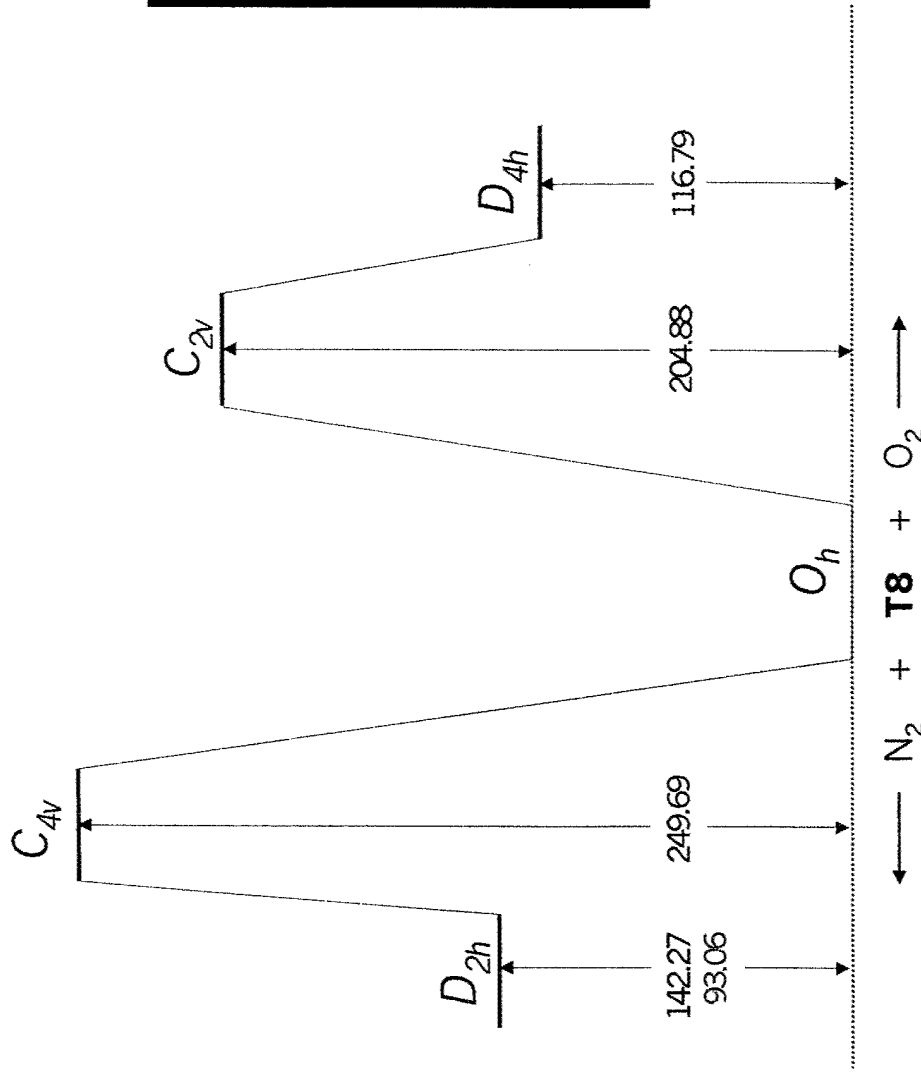




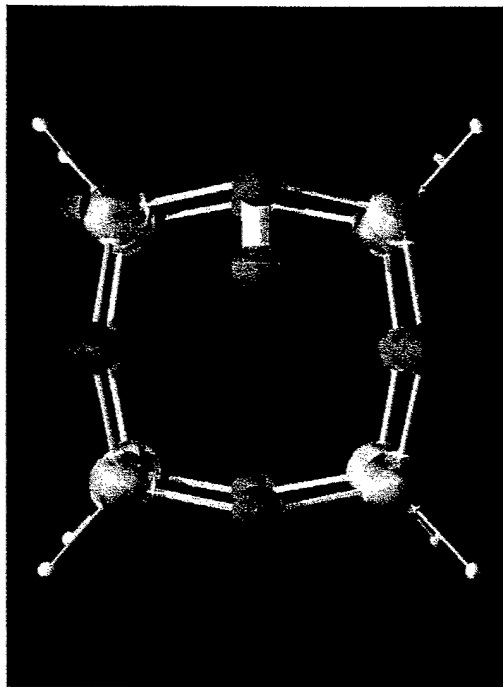
# RESULTS - POSS



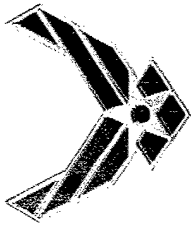
## Molecular "sieves": preferential capture $N_2$ vs. $O_2$ ?



TS structure of  $T_8 + O_2$



$T_{10}$  and  $T_{12}$  calculations in progress  
HPC requirements: ~50,000 node-  
hrs, AHPARC T3E, 256 GB



# RESULTS - NLO

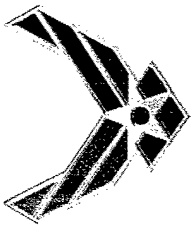


## B3LYP $S_0-T_1$ Excitation Energies (in eV)

System	6-31G(d)	Error	Exp
Porphyrin ( $1^3B_{2u}$ )	1.42	0.16	1.58 <sup>a</sup>
Zinc Porphyrin ( $1^3B_{1u}$ )	1.65	0.07	1.72 <sup>b</sup>
Tetraphenylporphyrin ( $1^3B_1$ )	1.31	0.14	1.45 <sup>c</sup>
Zinc Tetraphenylporphyrin( $1^3B_1$ )	1.53	0.06	1.59 <sup>d</sup>
Zinc Phthalocyanine ( $1^3B_{2u}$ )	1.05	0.08	1.13 <sup>e</sup>
Zinc Tetrabenzporphyrin ( $1^3B_{1u}$ )	1.41	0.16	1.57 <sup>f</sup>
Phthalocyanine ( $1^3B_{1u}$ )	1.18	0.06	1.24 <sup>g</sup>
Mean Error		0.10	

<sup>a</sup>Gouterman, Khalil, *J. Mol. Spectrosc.* 1974, 53, 88. (EPA (5:5:2) mixture of ethyl ether to isopentane to ethanol) and 50% ethyl iodide at 77 K) <sup>b</sup>Gradyushko, Tsvirko, *Opt. Spectrosc.* 1971, 31, 291.(EPA at 77 K) <sup>c</sup>Gouterman, Khalil, *J. Mol. Spectrosc.* 1974, 53, 88. (EPA at 77 K) <sup>d</sup>Walters et al., *J. Phys. Chem.* 1995, 99, 1166.(1:1 mixture of ether to ethanol at 77 K) <sup>e</sup>Vincett et al.,K. E. *J. Chem. Phys.* 1971, 55, 4131. (1-chloronaphthalene at 77 K) <sup>f</sup>Bajema, Gouterman, *J. Mol. Spectrosc.* 1971, 39, 421 (octane at 77 K) <sup>g</sup>McVie et al., *J. Chem. Soc. Faraday Trans. II* 1978, 74, 1870 (1-chloronaphthalene at 77 K)

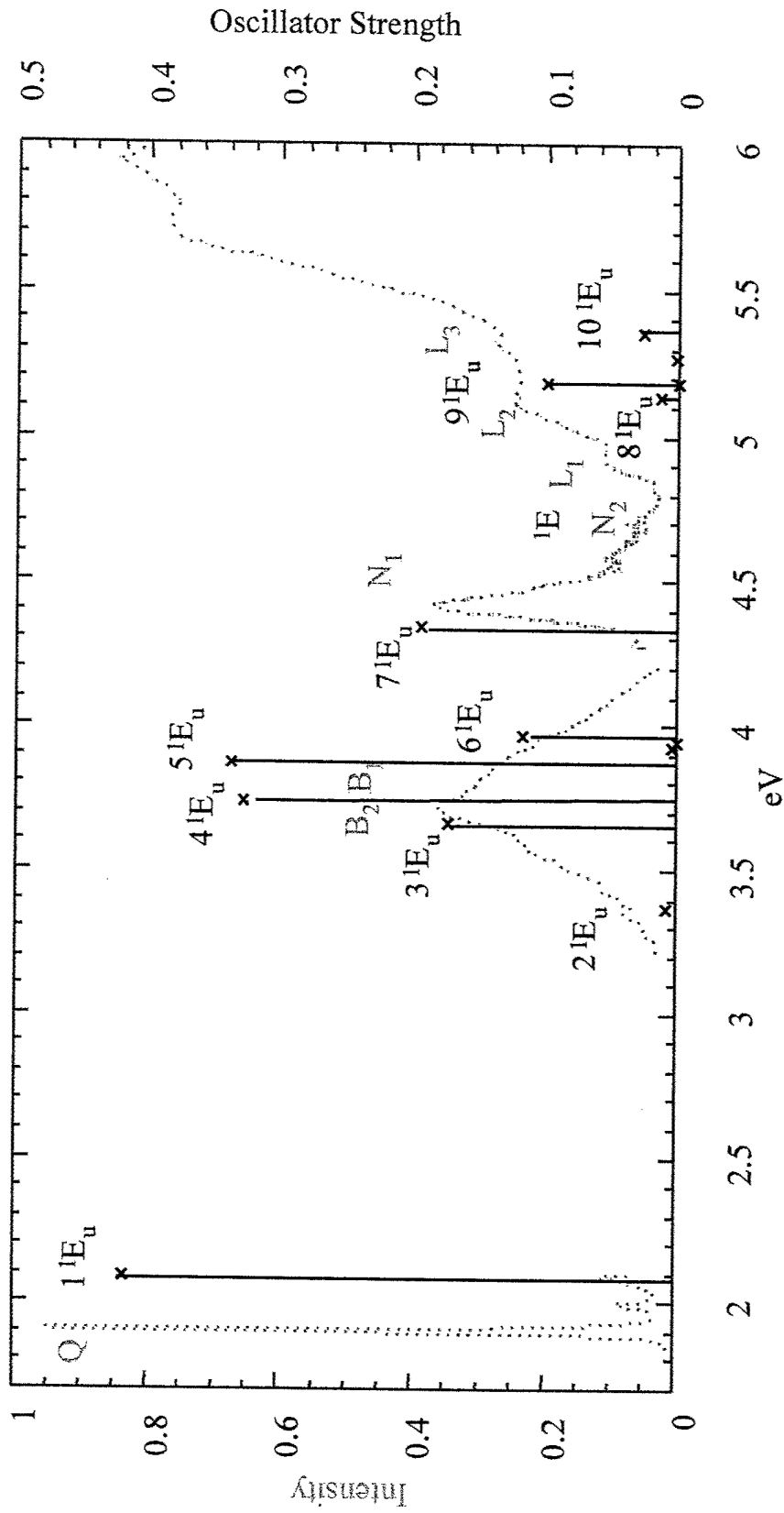
Nguyen, K. A., Day, P. N., and Pachter, R., *J. Chem. Phys.*, 110 (1999) 9135  
Nguyen, K. A., Day, P. N., and Pachter, R., *J. Phys. Chem. A*, 103 (1999) 7378  
Nguyen, K. A., Day, P. N., and Pachter, R., *J. Phys. Chem.*, 104 (2000) 4755  
Nguyen, K. A. and Pachter, R., *J. Phys. Chem.*, 104 (2000) 4549



# RESULTS - NLO



## Comparison with Experiment: ZnPc



HPC Requirements: ~100,000 CPU hours, on SGI O2K + IBM SP3 + SGI O2K @ ASC