

REPORT DOCUMENTATION PAGE

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1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE Technical Papers	3. DATES COVERED (From - To)
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	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

Please see attached

6. AUTHOR(S)	5d. PROJECT NUMBER 2303
	5e. TASK NUMBER m208
	5f. WORK UNIT NUMBER 345709
	8. PERFORMING ORGANIZATION REPORT

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048	8. PERFORMING ORGANIZATION REPORT
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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S NUMBER(S) please see attached

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

20030129 234

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT A	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Leilani Richardson
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (661) 275-5015

2303 0708

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-2002-118**
Jerry Boatz (PRSP) et al., "New Materials Design" (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: _____

Signature _____ Date _____

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

Comments: _____

Signature _____ Date _____

3. This request has been reviewed by the STINFO for: a.) changes if approved as amended, b) appropriateness of references, if applicable; and c.) format and completion of meeting clearance form if required

Comments: _____

Signature _____ Date _____

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: _____

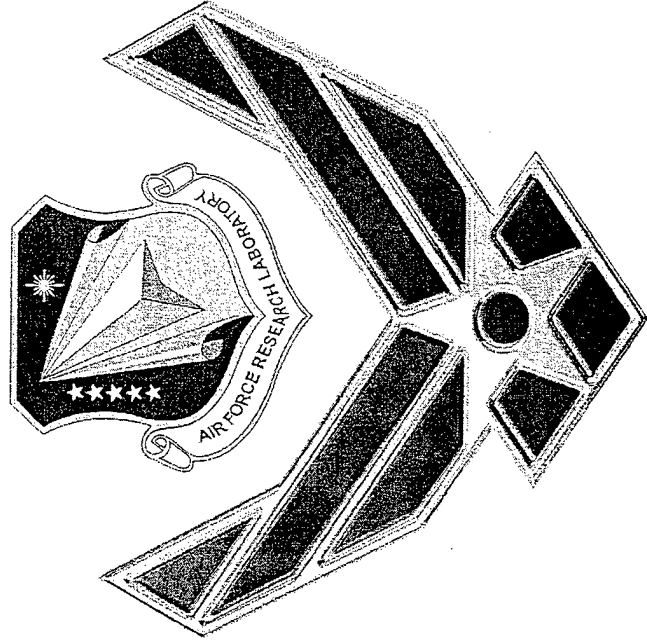
APPROVED/APPROVED AS AMENDED/DISAPPROVED

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

New Materials Design

DoD UGC, 10-14 Jun 02

Austin, TX

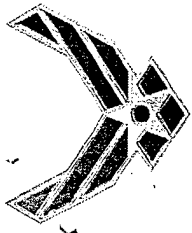


Jerry Boatz

Senior Research Chemist

Propulsion Directorate

Air Force Research Laboratory



NEW MATERIALS DESIGN



THE TEAM....

Prof. Mark S. Gordon

IOWA STATE UNIVERSITY

Prof. Gregory Voth

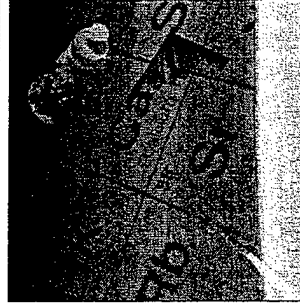


Prof. Sharon Hammes-Schiffer

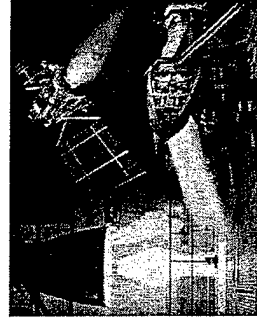
PENNSYLVANIA STATE UNIVERSITY

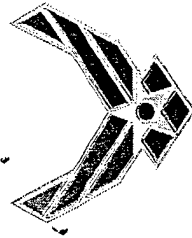


Dr. Ruth Pachter, AFRL/MLPJ



Dr. Jerry Boatz, AFRL/PRSP





OUTLINE



1. Project Overview

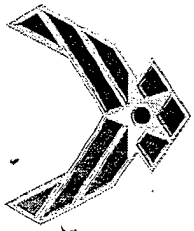
- High energy density matter
- Polyhedral oligomeric silsesquioxanes (POSS)
- Non-linear optical materials

2. Theoretical Methods and benchmarks

- Ab initio electronic structure theory
- Nuclear-electronic orbital approach
- Centroid Molecular Dynamics

3. Results

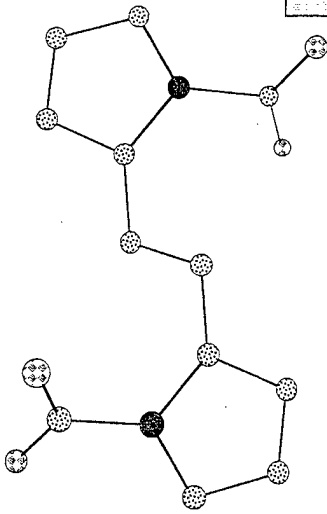
4. Summary



PROJECT OVERVIEW - HEDM



High Energy Density Matter -- next generation rocket propellants

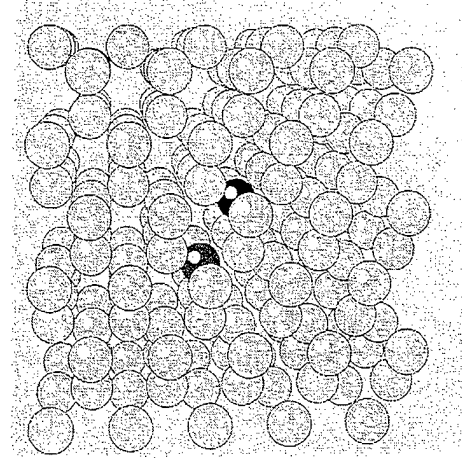


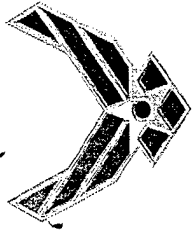
High-nitrogen/poly-nitrogen compounds

Specific Impulse

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

Atom-doped solid hydrogen





PROJECT OVERVIEW - HEDM



Technical issues being addressed using CCM

1. High-nitrogen/polynitrogen compounds

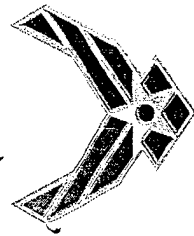
Objective: identify, characterize, and synthesize stable compounds with high heats of formation, high densities

- structures, energy content, stabilities, reaction pathways

2. Energetic atoms in solid hydrogen

Objective: stabilize ~5% energetic atoms in solid hydrogen

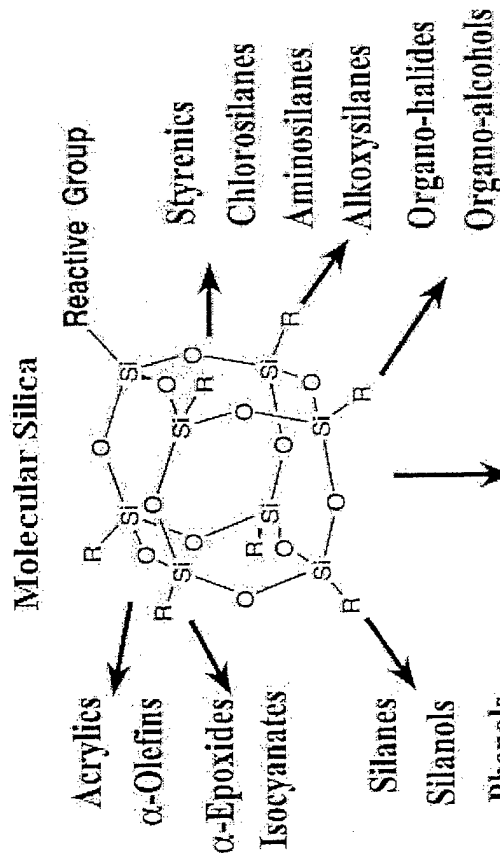
- stabilities, mobilities, concentration limits of atoms stored in hydrogen matrices



PROJECT OVERVIEW - POSS



Polyhedral oligomeric silsesquioxanes -- next generation plastics



As Additives

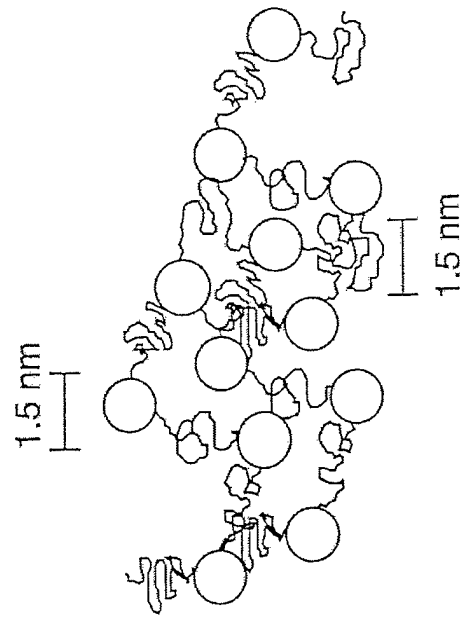
Heat/abrasion resistant paints and coatings
Mechanical property/viscosity/thermal modifiers
Crosslinking agents
Fire retardants

As Plastics

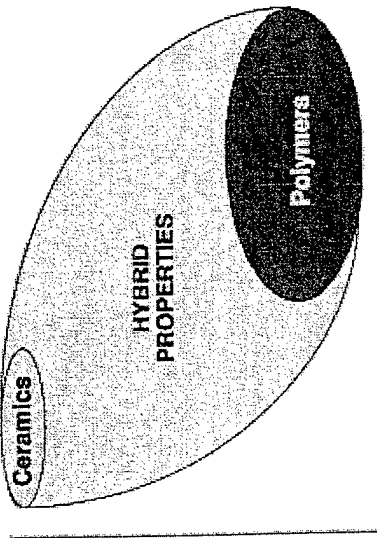
Medical materials
Space resistant resins
Packaging/coatings
Electronic materials
Optical Plastics

As Preceramics

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

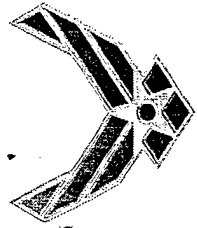


HYBRID POLYMERS



Use
Temperature

Toughness



PROJECT OVERVIEW - POSS



Technical issues being addressed using CCM

1. Mechanisms of formation

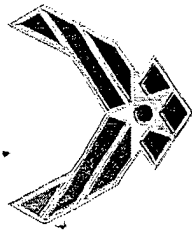
Objective: rational design and synthesis of POSS

- 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

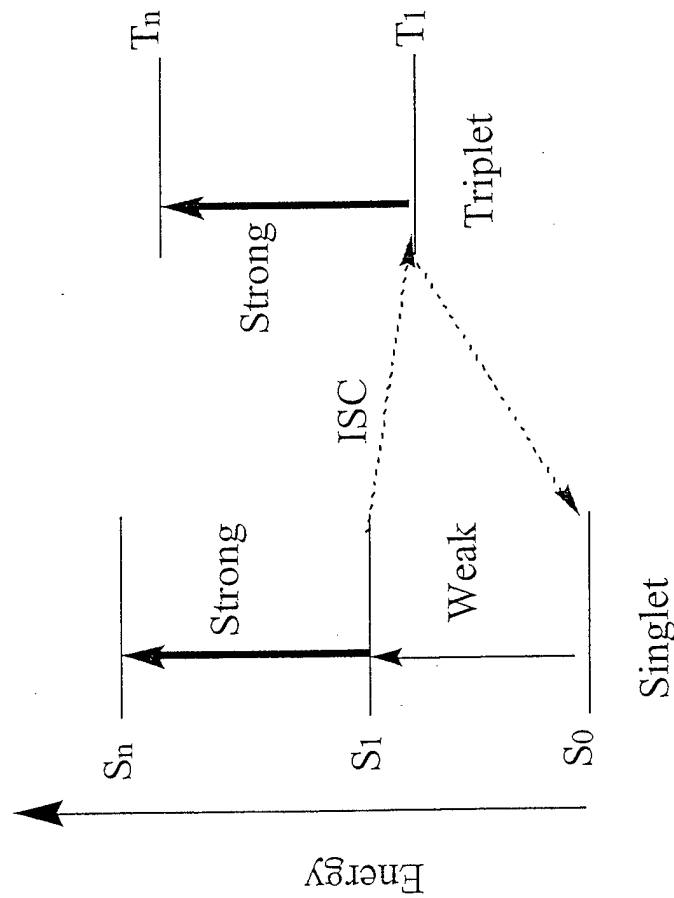


PROJECT OVERVIEW - NLO



Technical issues being addressed using CCM

1. Mechanism of reverse saturable absorption (RSA)



Key Components of RSA

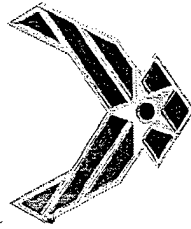
Ground state spectra (linear response)

Singlet-triplet splittings (ISC, phosphorescence)

Ionization potential (photoionization)

Excited triplet spectra (NLA)

Five-level model for nonlinear absorption

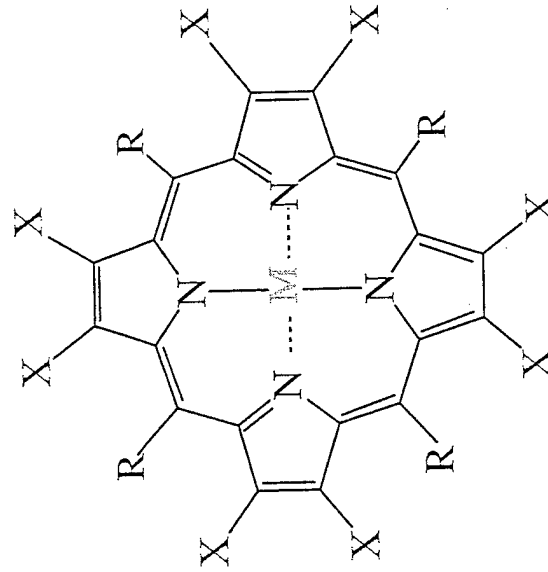


PROJECT OVERVIEW - NLO



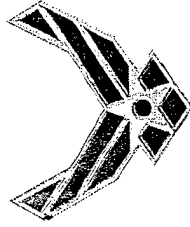
Technical issues being addressed using CCM

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



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

IP = Ionization Potential, S₀-S_n = Ground State Spectrum,
 S₀-T₁ = Singlet-Triplet Gap T₁-T_n = Triplet-Triplet Spectrum
 E = Experiment, C = Calculated



THEORETICAL METHODS



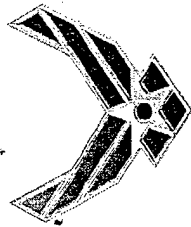
1. Ab initio electronic structure theory
 - General Atomic and Molecular Electronic Structure System (GAMESS) -- a CHSSI code
 - Nuclear-electronic orbital approach (NEO) for including nuclear quantum effects (important, e.g., in proton transfer reactions)

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

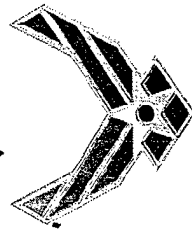


1. Ab initio electronic structure theory (cont.)
 - Most electronic structure codes use Born-Oppenheimer (i.e., “clamped nuclei”) approximation -- NOE method treats specified nuclei at QM level.

Nuclear-Electronic Hamiltonian

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

- 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	-	cp
MP2 gradient	cdp	-	cd	-	-
CI energy	cdp	cdp	-	cdp	cdp
CI gradient	cd	-	-	-	-
DFT energy	cdp	cdp	cdp	-	-
DFT gradient	cdp	cdp	cdp	-	-

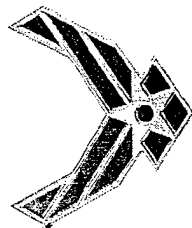
c = conventional disk storage of AO integrals

d = direct evaluation of AO integrals

p = runs in parallel



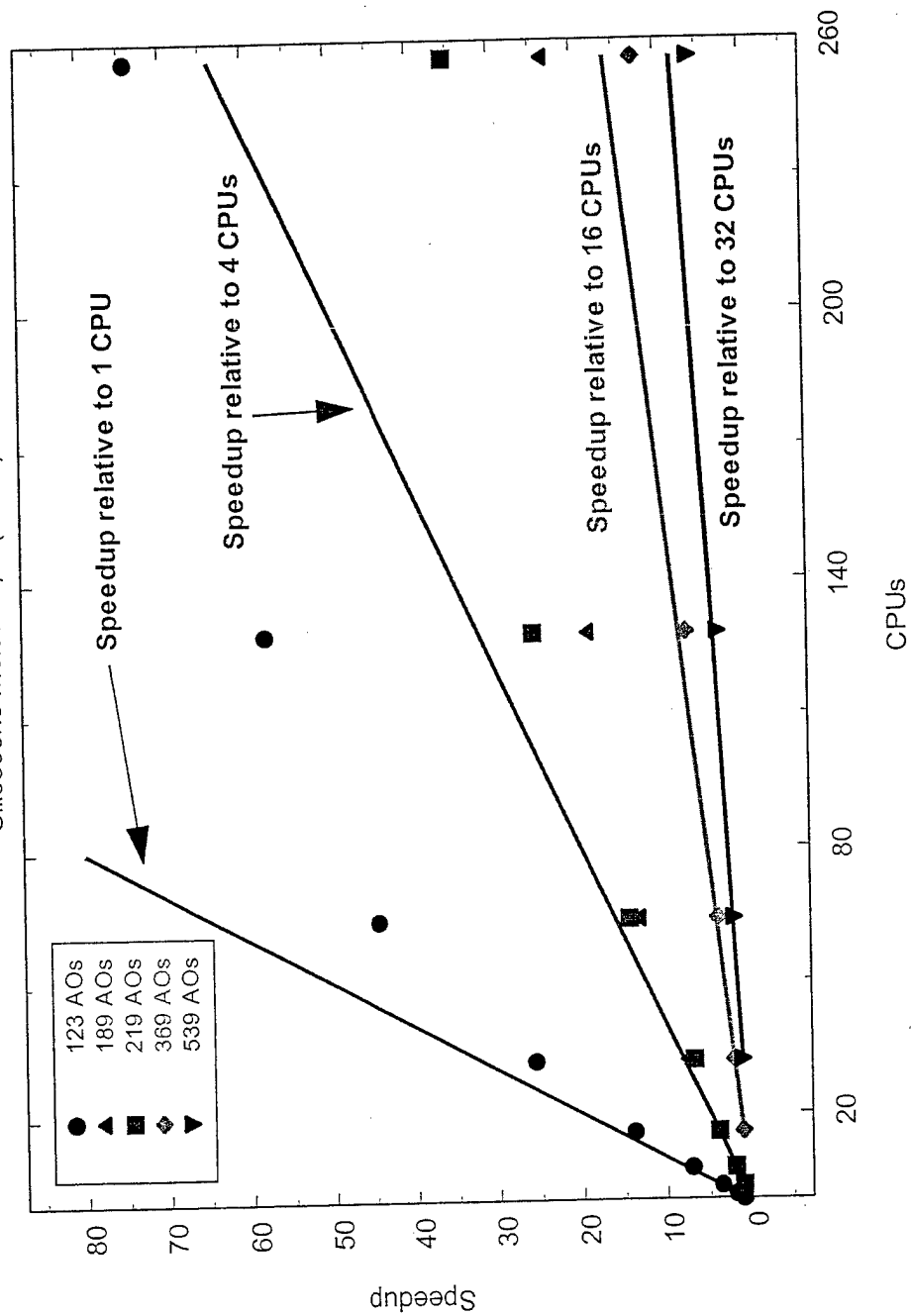
THEORETICAL METHODS

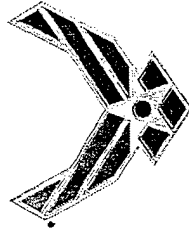


Ab initio electronic structure theory

MP2 Gradient Scalability Test

Silicocene molecule, Si(C₅H₅)₂



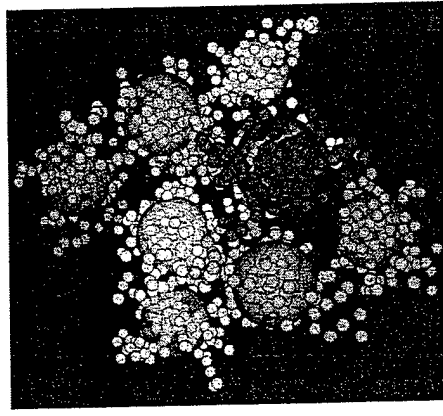
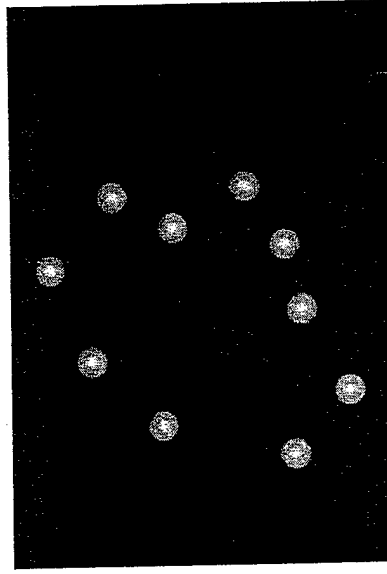
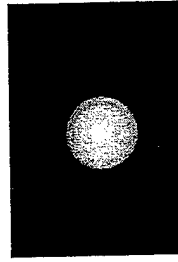


THEORETICAL METHODS

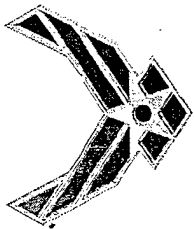


Path Integral Molecular Dynamics & Centroid Molecular Dynamics (CHSSI codes)

Simulation methods based on path integral techniques for mapping quantum particles onto “polymer ring” of classical quasiparticles:



Each “real” particle is replaced by N ($50 < N < 500$) quasiparticles; classical dynamics done on collection of quasiparticles \Rightarrow natural, efficient parallelism.

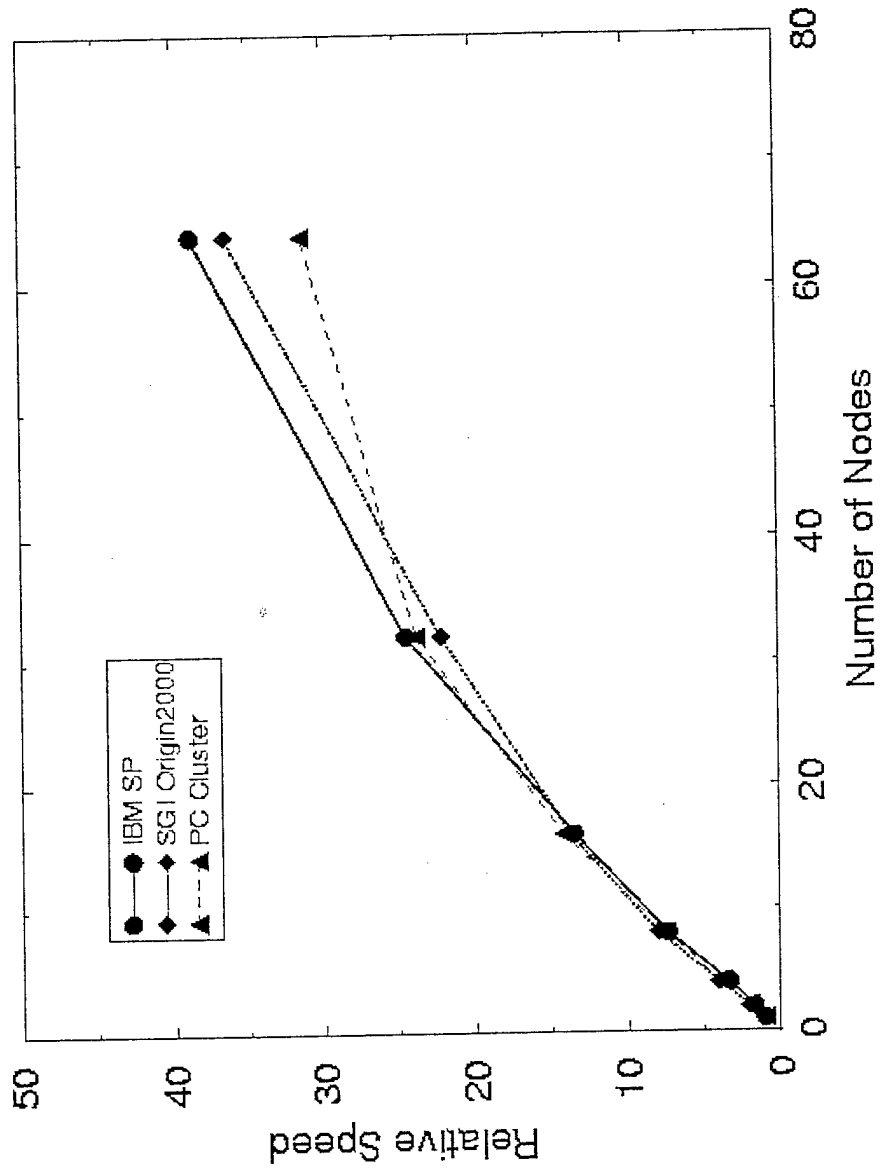


THEORETICAL METHODS



Path Integral Molecular Dynamics & Centroid Molecular Dynamics

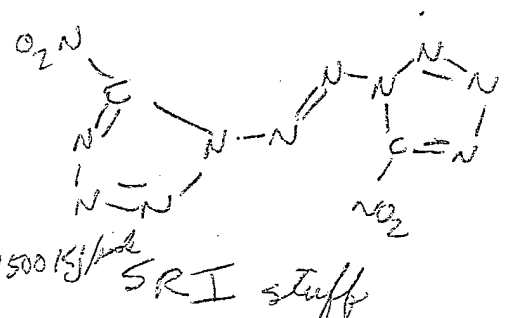
Code Scaling



Input>rocket, chamber, 20.410000, exhaust, 0.010000

Rocket specific impulse calculation:

The chamber pressure = 20.41 atm
The exhaust pressure = 0.01 atm
The initial equation error was huge: 24728.149173



The Chamber State:

$\Delta H_f = +1500 \text{ kJ/kg}$
SRI stuff

Reference state = reactants
H(R) = H-1773.07, E(R) = E-1773.05, S(R) = S- 0.00

	P (ATM)	V (CC/GM)	T (K)	H(R) (CAL/GM)	E(R) (CAL/GM)	S(R) (CAL/K/GM)	VGS (CC/GM)
1.)	20.4	909.6888	6436.6	0.00	-449.64	2.389	909.6888

Product concentrations

Name	(mol/kg)	(mol gas/mol explosive)
n2 Gas	2.112e+001	5.410e+000
co Gas	7.734e+000	1.981e+000
no Gas	4.609e+000	1.180e+000
o2 Gas	1.561e+000	3.998e-001
co2 Gas	7.513e-002	1.924e-002
no2 Gas	1.418e-003	3.632e-004
*c solid	0.000e+000	0.000e+000
Total Gas	3.510e+001	8.990e+000
Total Cond.	0.000e+000	0.000e+000

The Exhaust State:

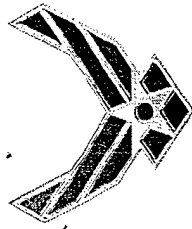
Reference state = reactants
H(R) = H-1773.07, E(R) = E-1773.05, S(R) = S- 0.00

	P (ATM)	V (CC/GM)	T (K)	H(R) (CAL/GM)	E(R) (CAL/GM)	S(R) (CAL/K/GM)	VGS (CC/GM)
1.)	0.0	565350.1813	2148.9	-1863.53	-2000.43	2.389565350.1813	

Product concentrations

Name	(mol/kg)	(mol gas/mol explosive)
n2 Gas	2.337e+001	5.984e+000
co2 Gas	6.157e+000	1.577e+000
co Gas	1.652e+000	4.232e-001
o2 Gas	7.645e-001	1.958e-001
no Gas	1.234e-001	3.160e-002
no2 Gas	5.283e-006	1.353e-006
*c solid	0.000e+000	0.000e+000
Total Gas	3.206e+001	8.212e+000
Total Cond.	0.000e+000	0.000e+000

The specific impulse = 402.54 seconds



RESULTS - HEDM



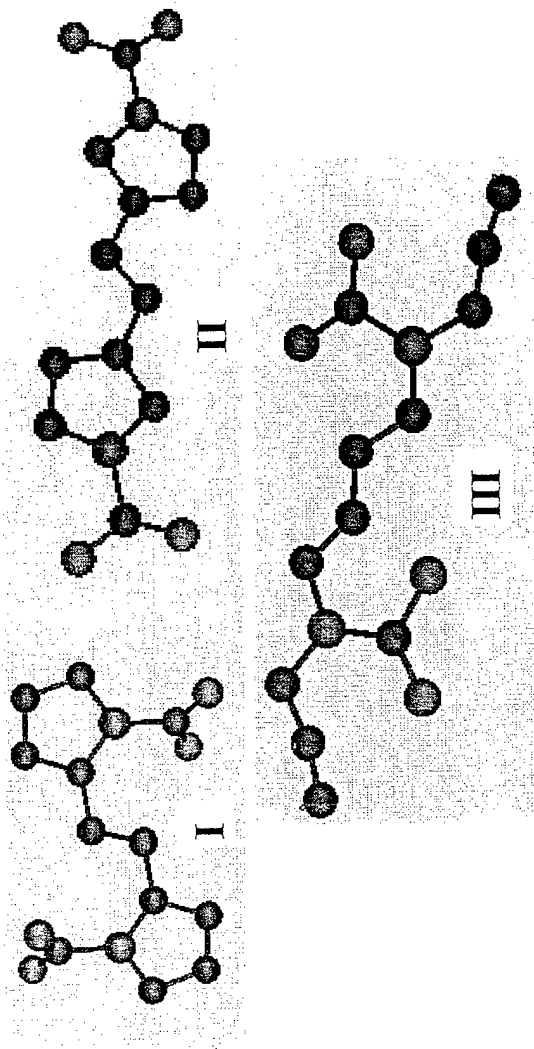
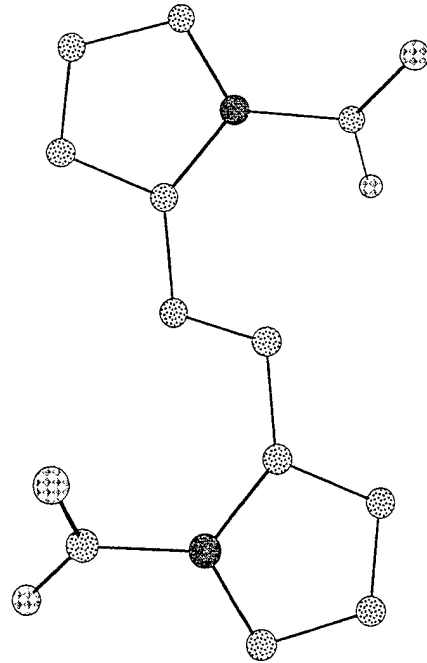
High-nitrogen/polynitrogen compounds

Predicted $\Delta H_f = 457$ kcal/mol, $I_{sp} = 329$ sec (sea level)

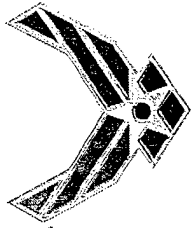
(I_{sp} for hydrazine = 233 sec)

Relative energies (kcal/mol)

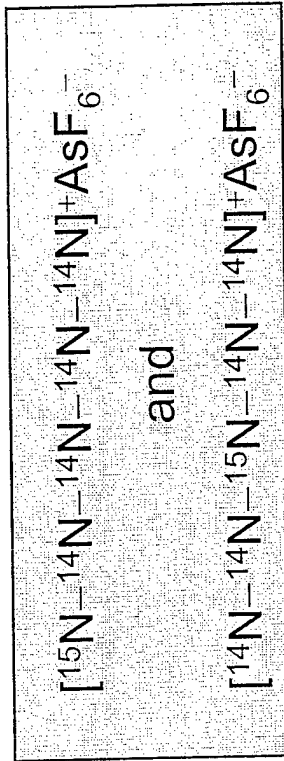
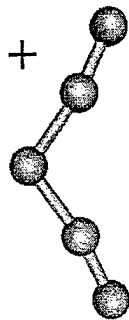
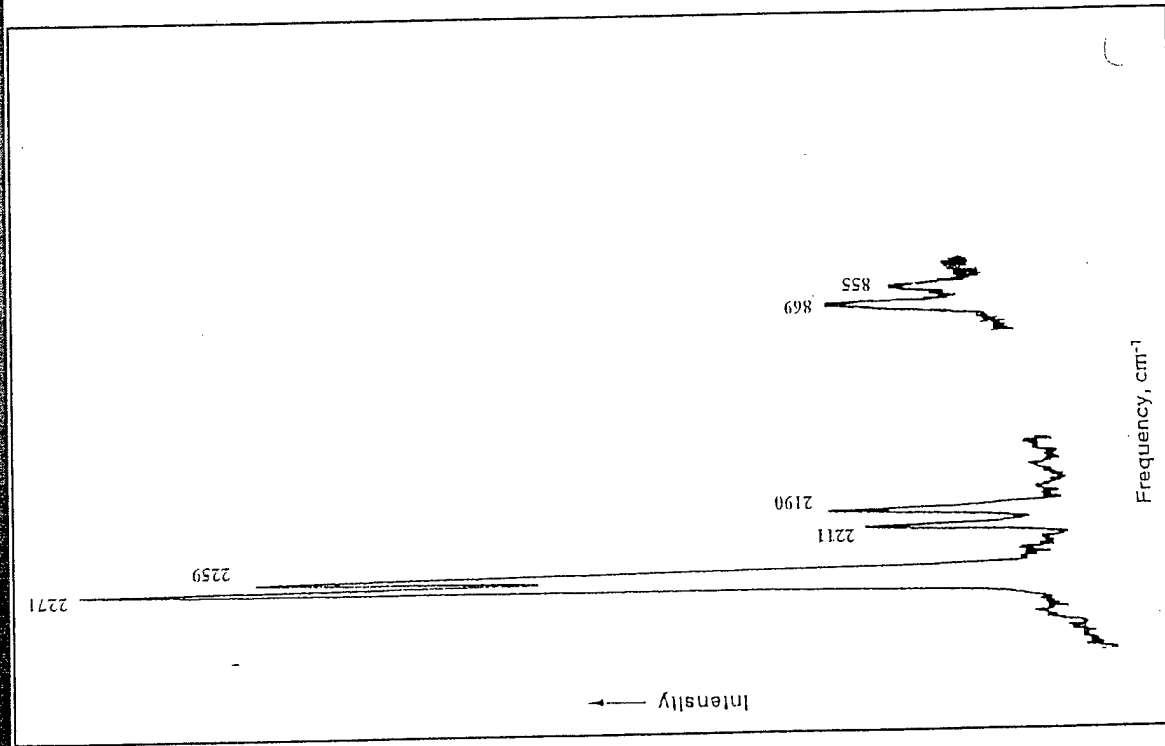
I: 0 II: -15 III: +36



Computational requirements: 4500 MW memory, ~350,000 node-hrs, ERDC T3E



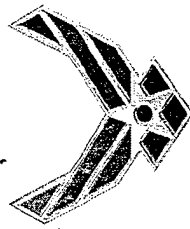
Identifying a Completely New Molecule: Comparison of Calculated and Measured Spectra



¹⁴N - ¹⁵N Isotopic Shifts (cm⁻¹)

Mode	Obs.	Calc.†
$\nu_1(a_1)$	12	11.8
$\nu_7(b_2)$	21	21.4
$\nu_2(a_1)$	14	14.1

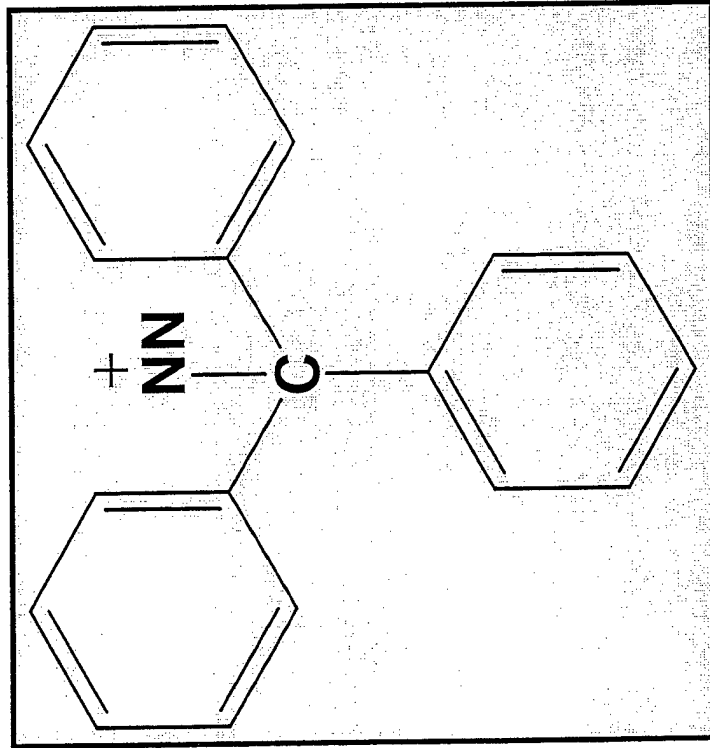
†CCSD(T)/6-311+G(2d) results



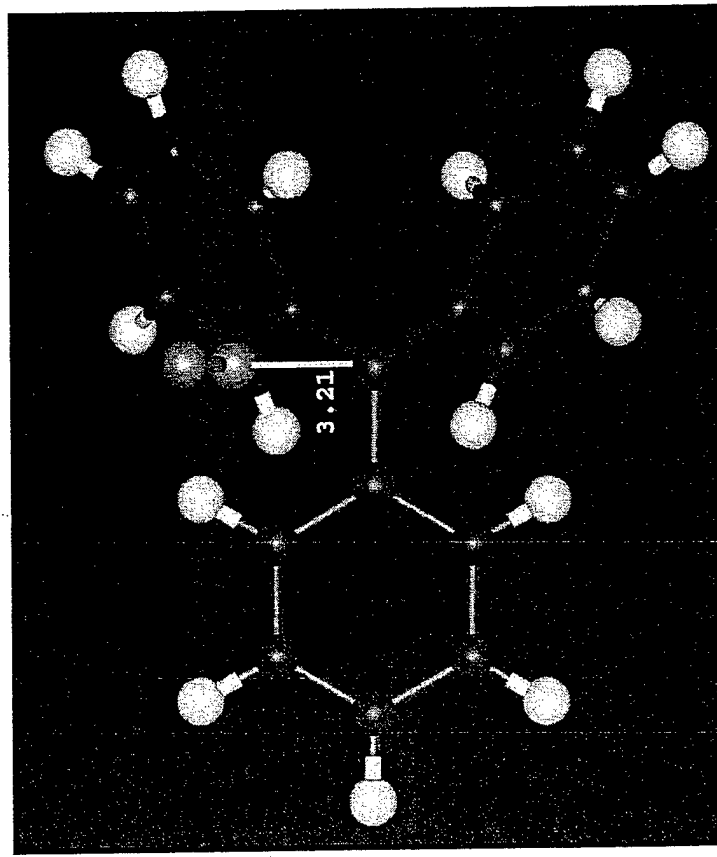
Identifying Precursors for New Polynitrogens



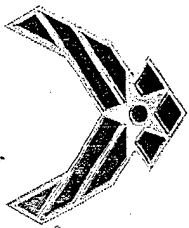
*This ion has been suggested
as a useful precursor to new
polynitrogen molecules...*



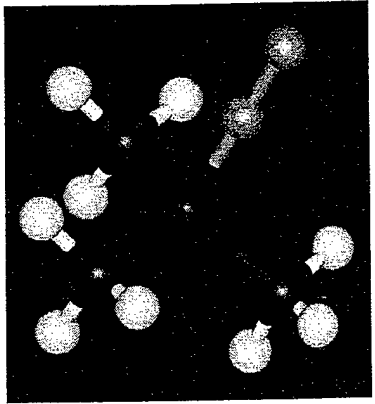
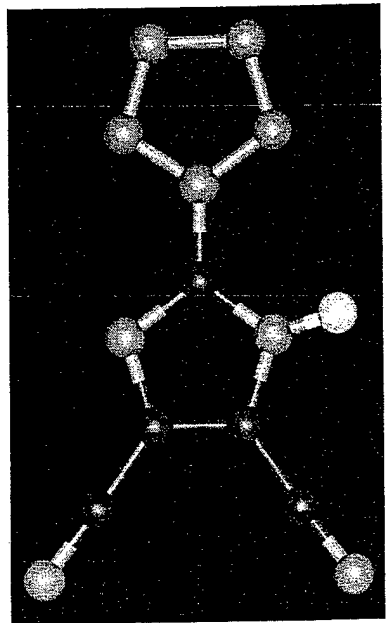
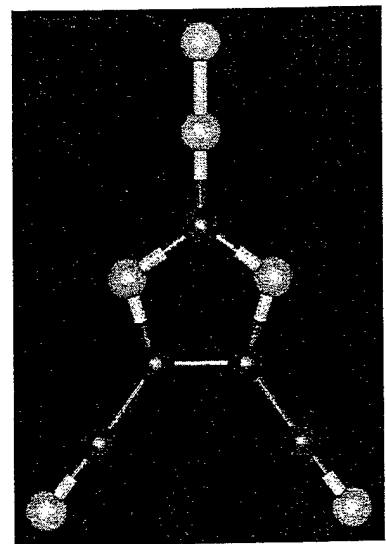
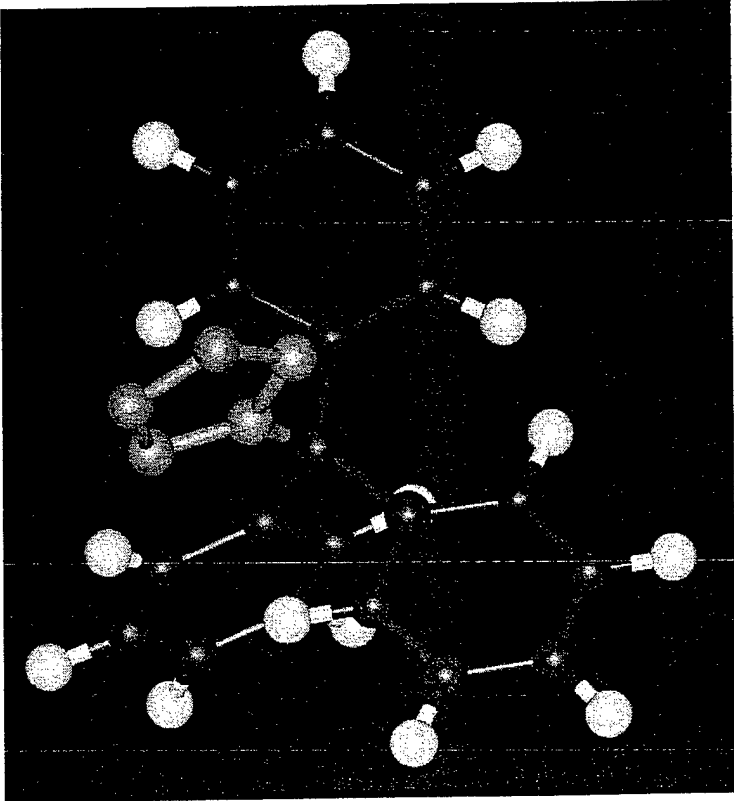
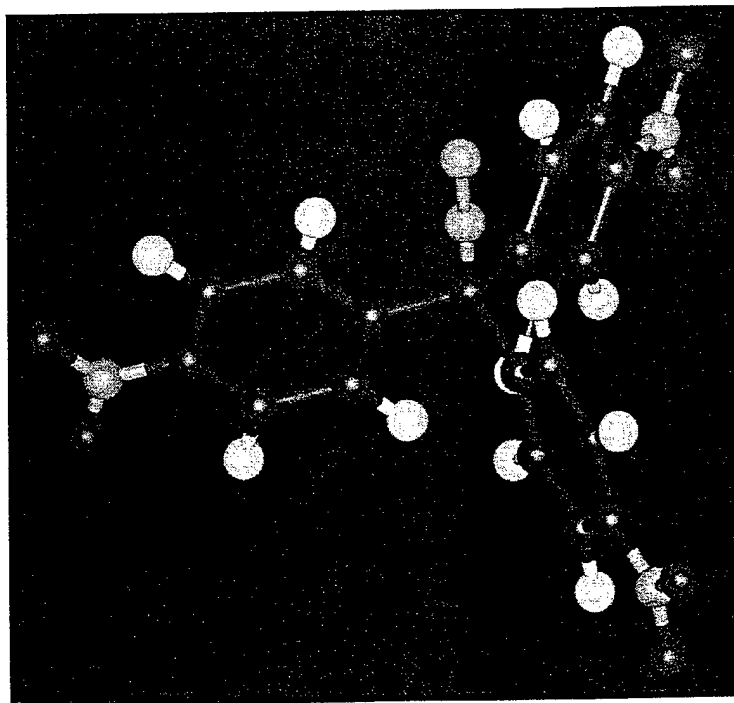
*... but calculations predict it to be
unstable.*

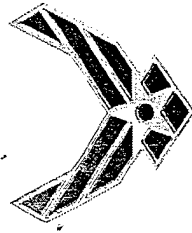


Computational requirements: ~10,000 CPU-hours, 1200 MW on IBM SP/P3 at ASC



Other Potential Polynitrogen Precursors Being Investigated





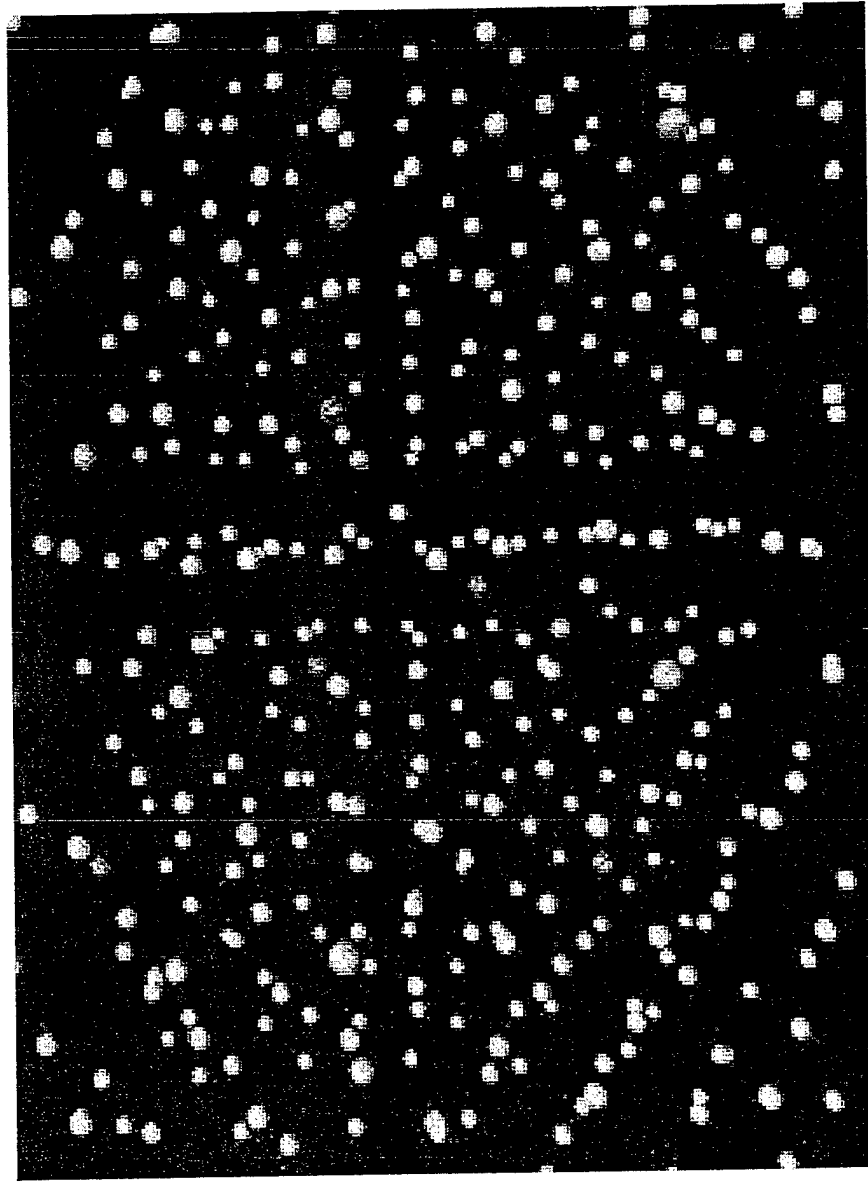
Atom-Doped Solid Hydrogen



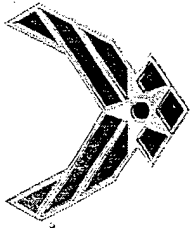
6.25% B atoms in solid *para*-H₂

Previous key results

1. In sH₂, B atoms more stable than Li atoms
2. No recombination of B atoms seen at concentrations up to 6.25%.
3. “Forced” recombination of B atoms does not trigger phase separation.



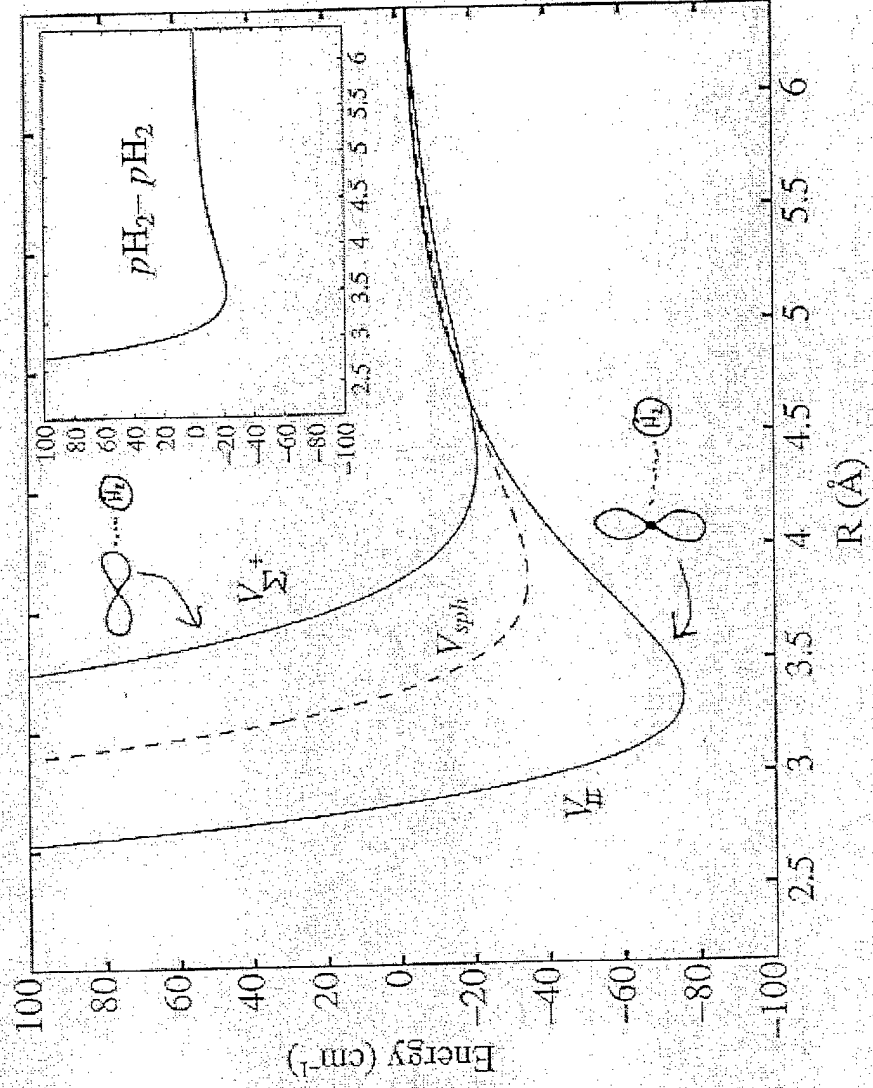
Computational requirements: ~50,000 CPU-hrs, MHPCC IBM SP

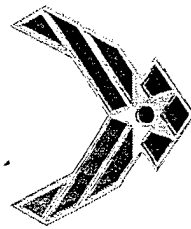


Atom-Doped Solid Hydrogen



How important is the orientational dependence of B-H₂ (Al-H₂) interactions in B/sH₂ (Al/sH₂)?

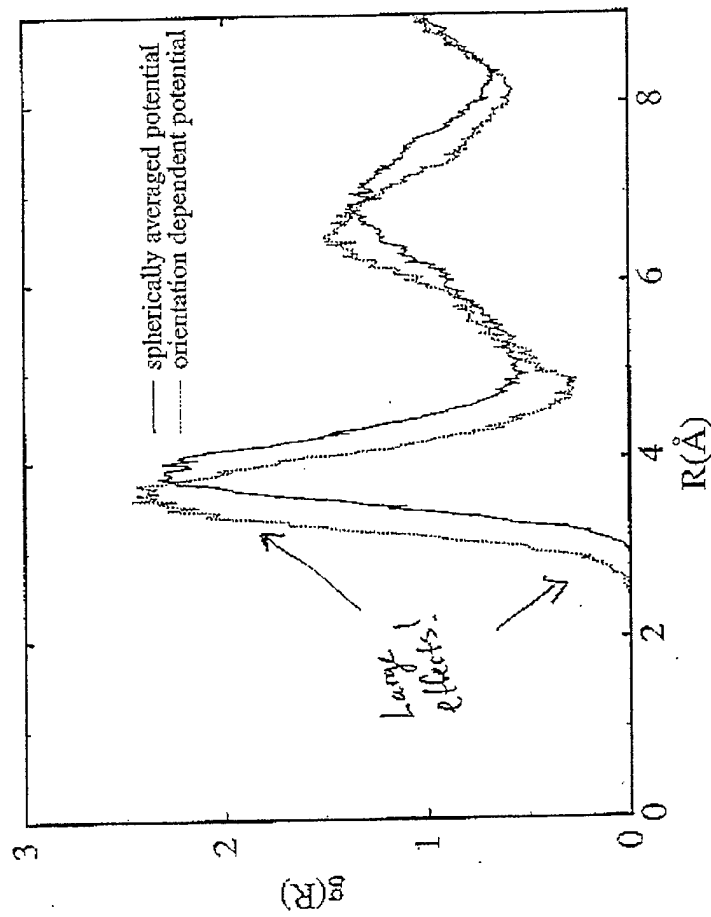




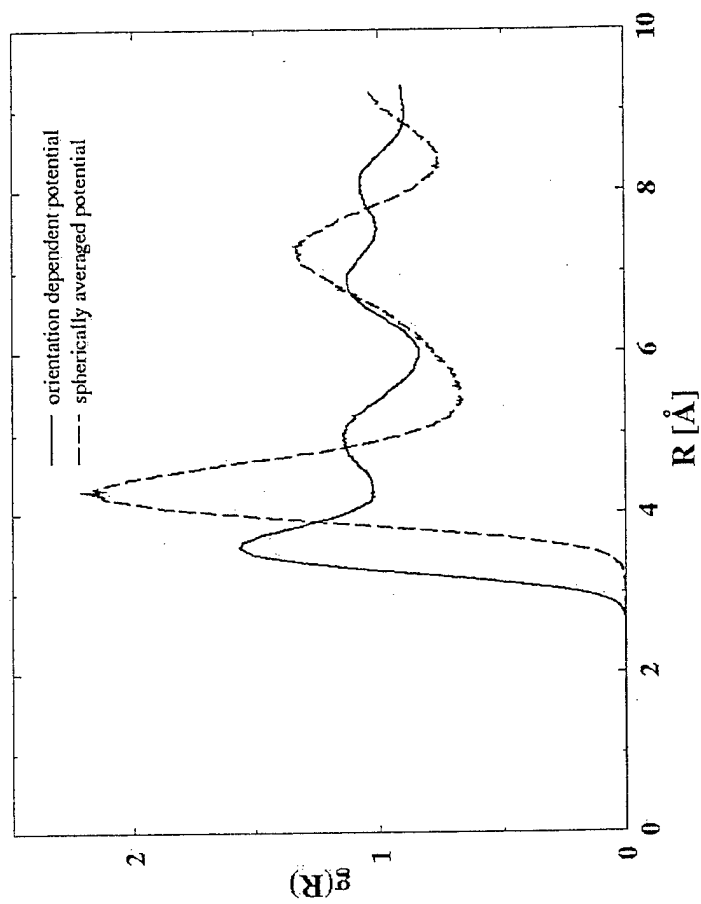
Atom-Doped Solid Hydrogen



B-H₂ pair correlation function



Al-H₂ pair correlation function





Atom-Doped Solid Hydrogen

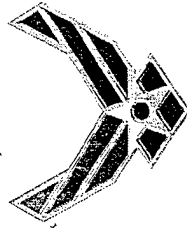


B-H₂ and Al-H₂ interaction energies (cm⁻¹)

	$\langle V_{B-H_2} \rangle$	$\langle V_{Al-H_2} \rangle$
Orientation dependent	-546.72 (1.92)	-263.41 (3.33)
Impurity no defect Spherically averaged	-443.32 (1.92)	-177.37 (1.26)
Orientation dependent	-538.49 (6.06)	-273.86 (2.37)
Impurity & defect Spherically averaged	-439.88 (3.56)	-179.52 (1.90)

Krumrine, J.R., Jang, S., Alexander, M.H., and Voth, G.A., J. Chem. Phys. 113 (2000) 9079

Mirjaniyan, D.T., Alexander, M.H., and Voth, G.A.: To be published



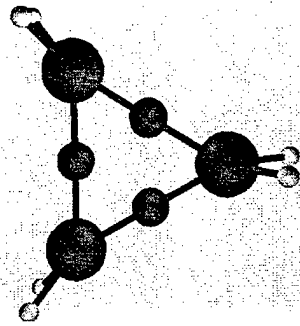
RESULTS - POSS



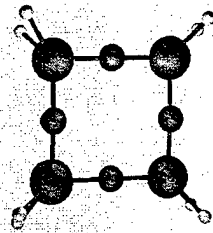
Mechanism of formation

Key steps

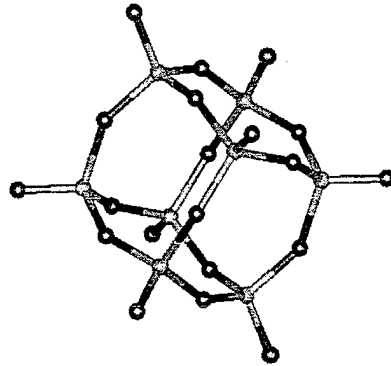
1. Hydrolysis of RSiX_3 ($\text{R}=\text{H}, \text{CH}_3, \text{t-butyl}, \text{etc.}; \text{X}=\text{Cl}$)
 $\text{RSiCl}_3 + \text{H}_2\text{O} \rightarrow \text{RSiCl}_2\text{OH} + \text{HCl}$
 $\text{RSiCl}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{RSiCl(OH)}_2 + \text{HCl}$
 $\text{RSiCl(OH)}_2 + \text{H}_2\text{O} \rightarrow \text{RSi(OH)}_3$
2. Condensation of 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 D_3, 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 D_3, D_4 to POSS (in progress)
 $2\text{D}_4 \rightarrow \text{T}_8 + 4\text{H}_2\text{O}$
....



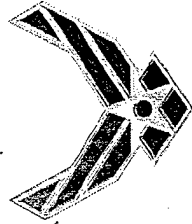
D3



D4



T8



RESULTS - POSS

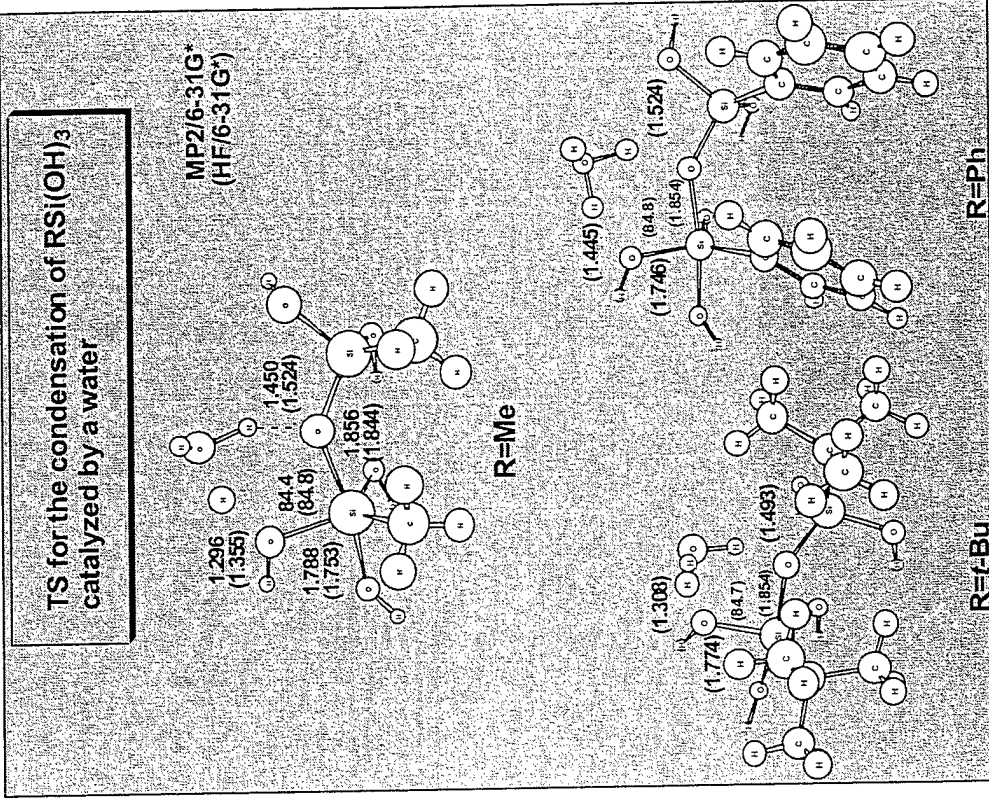


Mechanism of formation: role of solvent (H₂O) & substituents (R)

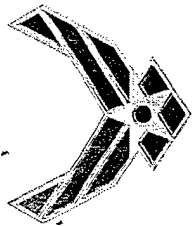
$R\text{Si}(\text{OH})_3 + R\text{Si}(\text{OH})_3 \rightarrow R(\text{OH})_2\text{SiOSi}(\text{OH})_2R + \text{H}_2\text{O}$

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.



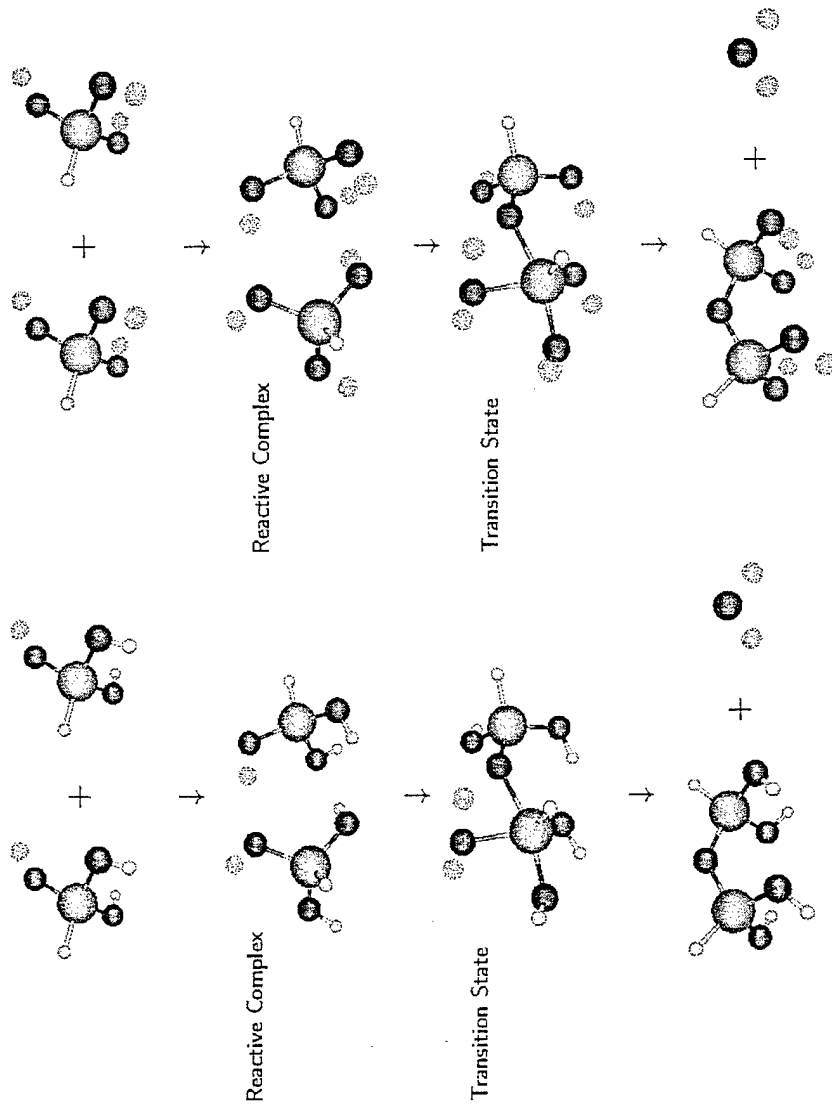
Kudo, T., Gordon, M.S. J. Am. Chem. Soc., 120, 11432 (1998)
 Kudo, T., Gordon, M.S. J. Phys. Chem. A, 104, 4058 (2000)



RESULTS - POSS

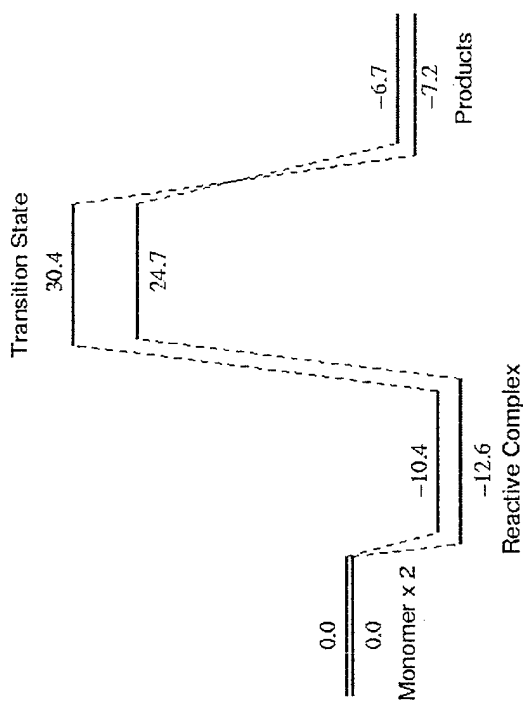


Nuclear quantum effects in condensation reactions



Level	Monomer $\times 2$	Reactive Complex	Transition State	Products	CPU Time
RHF/6-31G*	0.0	-10.4	30.4	-7.2	1.0
NEO-HF/2	0.0	-11.4	24.9	-5.9	1.1
NEO-HF/6	0.0	-12.6	24.7	-6.7	1.8

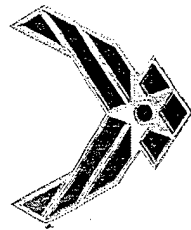
Units in kcal/mol



Hammes-Schiffer, S., J. Phys. Chem. A 102 (1998), 10443

Webb, S.P., Agarwal, P.K., and Hammes-Schiffer, S., J. Phys. Chem. B 104(2000), 888

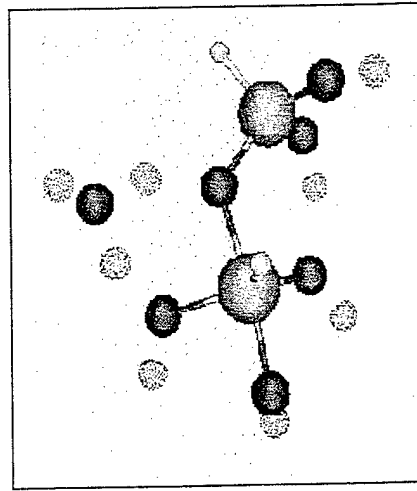
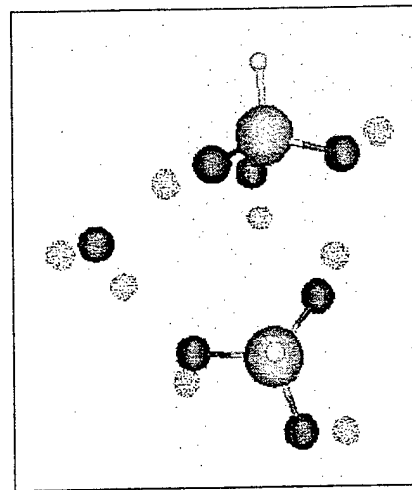
Webb, S.P. and Hammes-Schiffer, S., J. Chem. Phys. 113 (2000), 5214



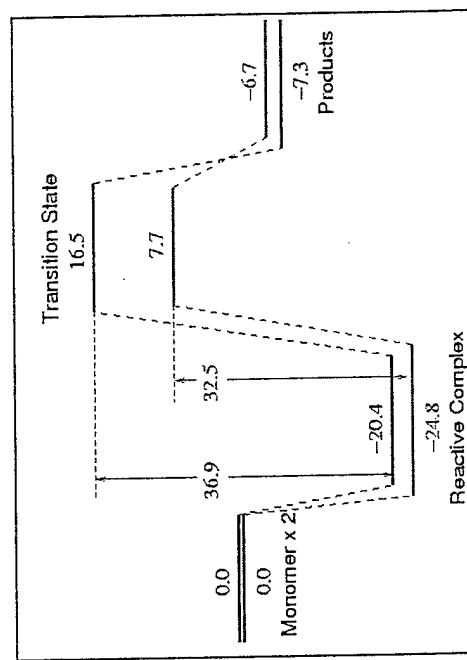
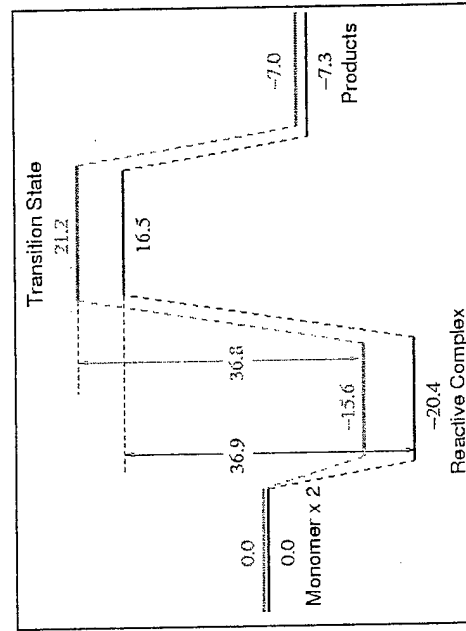
RESULTS - POSS

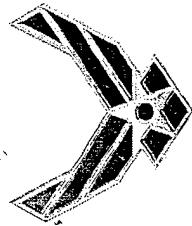


Nuclear quantum effects in water-catalyzed condensation reactions



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

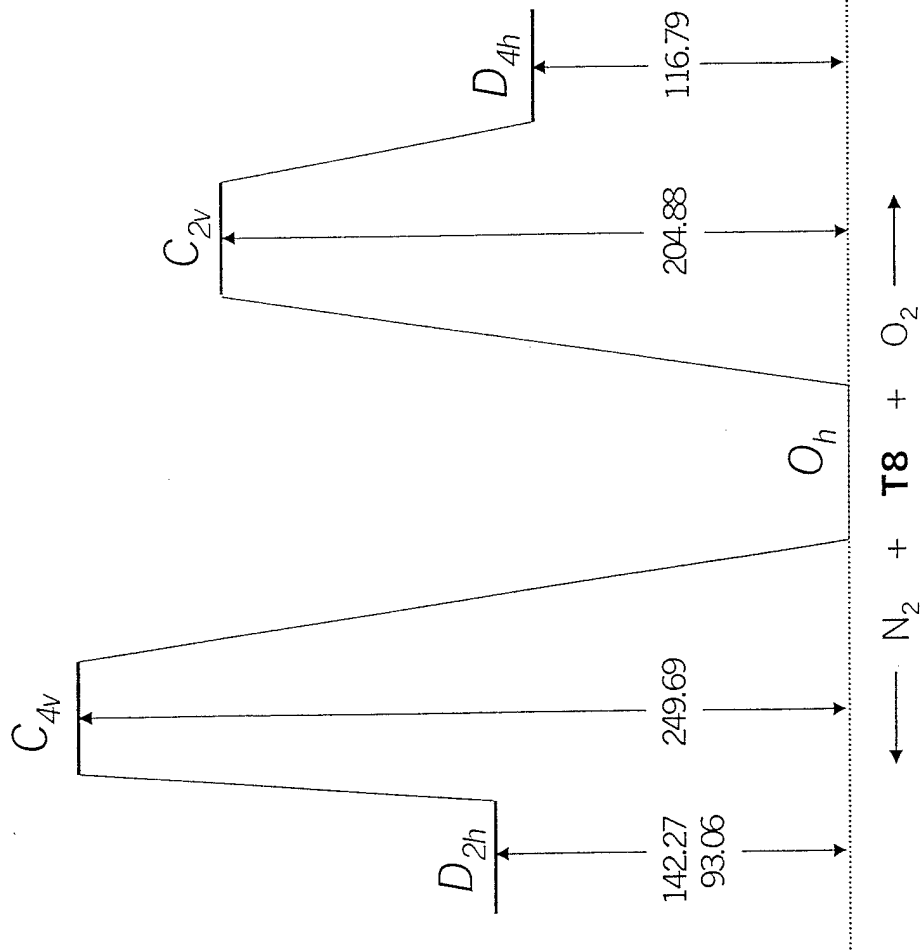




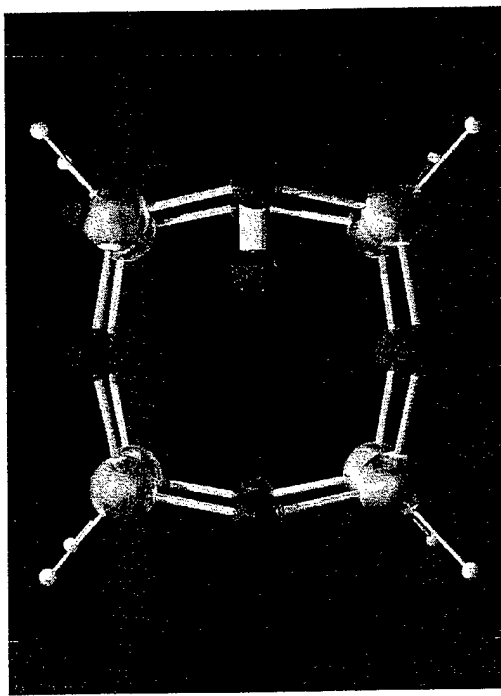
RESULTS - POSS



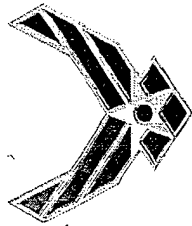
Molecular "sieves": preferential capture N_2 vs. O_2 ?



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

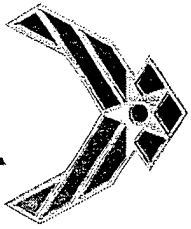


B3LYP S_0 - T_1 Excitation Energies (in eV)

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

^aGouterman, 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) ^bGradyushko, Tsvirko, *Opt. Spectrosc.* 1971, 31, 291.(EPA at 77 K) ^cGouterman, Khalil, *J. Mol. Spectrosc.* 1974, 53, 88. (EPA at 77 K) ^dWalters et al., *J. Phys. Chem.* 1995, 99, 1166.(1:1 mixture of ether to ethanol at 77 K) ^eVincett et al., *K. E. J. Chem. Phys.* 1971, 55, 4131. (1-chloronaphthalene at 77 K) ^fBajema, Gouterman, *J. Mol. Spectrosc.* 1971, 39, 421 (octane at 77 K) ^gMcVie et al., *J. Chem. Soc. Faraday Trans. II* 1978, 74, 1870 (1-chloronaphthalene at 77 K)

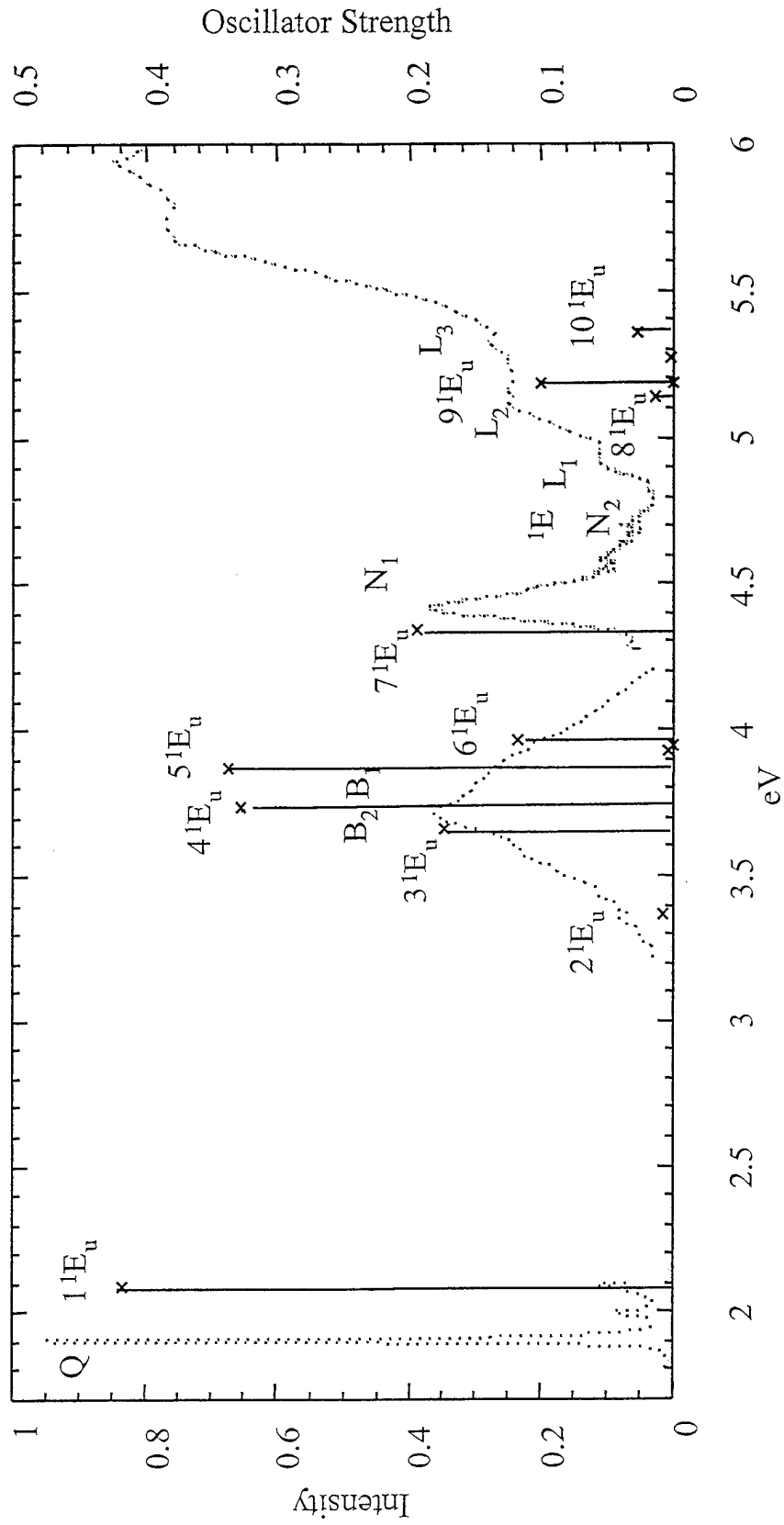
Nguyen, K. A., Day, P. N., and Pachter, R., *J. Chem. Phys.*, 110 (1999) 9135
Nguyen, K. A., Day, P. N., and Pachter, R., *J. Phys. Chem. A*, 103 (1999) 7378
Nguyen, K. A., Day, P. N., and Pachter, R., *J. Phys. Chem.*, 104 (2000) 4755
Nguyen, K. A. and Pachter, R., *J. Phys. Chem.*, 104 (2000) 4549



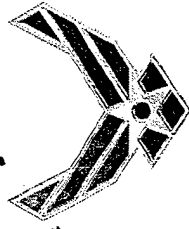
RESULTS - NLO



Comparison with Experiment: ZnPc



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



SUMMARY

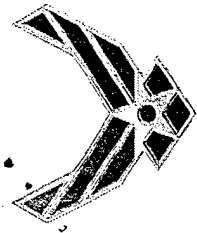


High Energy Density Matter

- High-nitrogen/polynitrogen compounds are more energetic than hydrazine.
- Trityldiazonium cation is not a stable polynitrogen precursor.
- Inclusion of anisotropic interactions of B, Al atoms in sH_2 predict greater stability than spherical interaction model.

Polyhedral Oligomeric Silsesquioxanes (POSS)

- Proton transfer reactions for hydrolysis and condensation are catalyzed by water.
- Alkyl substituents (R) in $RSiX_3$ have minor effects on hydrolysis and condensation reaction barriers.
- Nuclear quantum effects are important in proton transfer reactions --- lower barriers by >5 kcal/mol.
- T_8 is too small to encapsulate N_2 or O_2 .

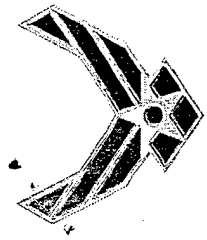


SUMMARY (cont.)



NLO materials

- Time-dependent density functional theory accurately predicts NLA in porphyrins.
- Computed triplet-triplet excitation energies within 0.1-0.4 eV of experiment
- Computed singlet-triplet excitation energies within 0.1-0.2 eV of experiment
- Computed ionization potentials accurate within 0.1 eV of experiment



ACKNOWLEDGEMENTS



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

HEDM: Millard Alexander, Jennifer Krumrine, Soomin Jang, Jeff Mills, Jeff Sheehy, Don Thompson, Dan Sorescu

NLO: Kiet Nguyen, Paul Day

GAMESS: Graham Fletcher

MSRCs, DCs: ASC, ARL, ERDC, NAVO, MHPCC, AHPCRC, ARSC, AFFTC

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