New Materials Design

DoD UGC, 18-21 Jun 01

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NEW MATERIALS DESIGN

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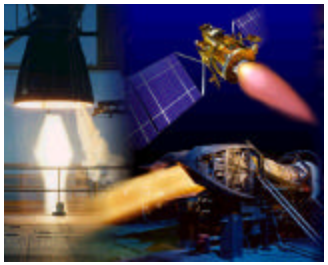


OUTLINE

1. **Project Overview**

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

2. **Theoretical Methods and benchmarks**

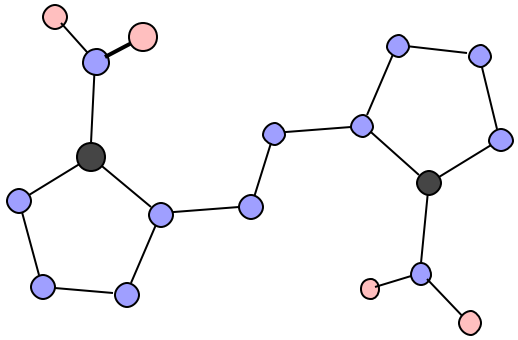
   - Ab initio electronic structure theory
   - Nuclear-electronic orbital approach
   - Centroid Molecular Dynamics

3. **Results**

4. **Summary**

PROJECT OVERVIEW - HEDM

High Energy Density Matter -- next generation rocket propellants

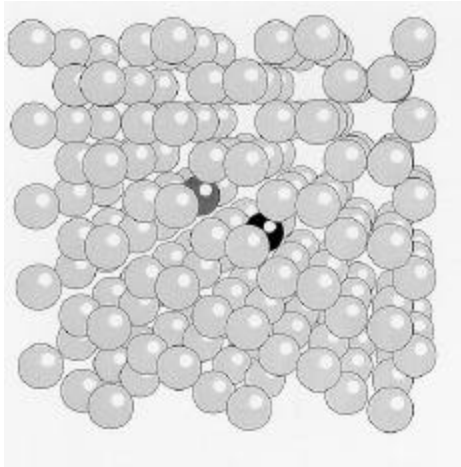


High-nitrogen/polynitrogen compounds

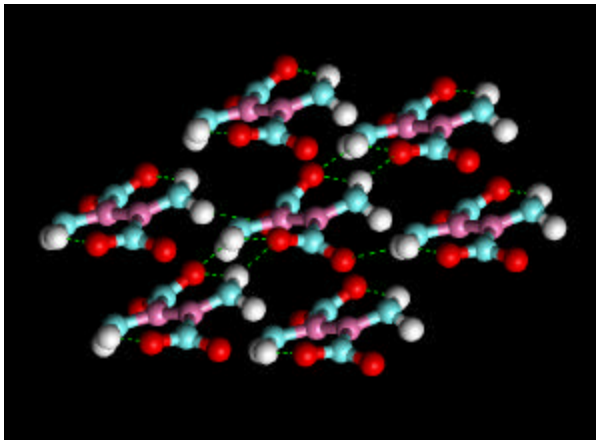
Specific Impulse

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

Atom-doped solid hydrogen



"FOX-7" (1,1-diamino-2,2-dinitroethylene)



PROJECT OVERVIEW - HEDM

Technical issues being addressed using CCM

1. High-nitrogen/polynitrogen compounds

Objective: identify, characterize, and synthesize <u>stable</u> 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

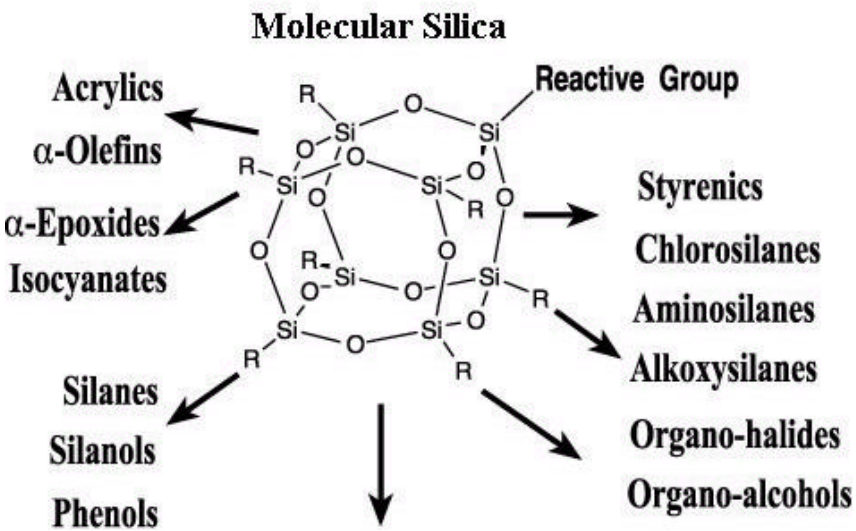
3. "FOX-7"

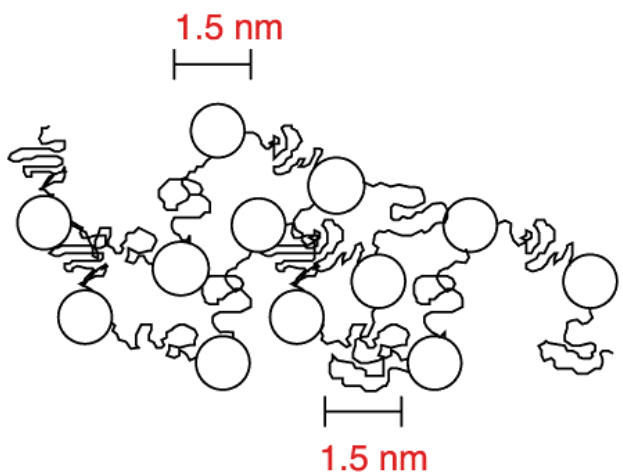
Objective: identify, characterize, and synthesize <u>stable</u> compounds with high heats of formation, high densities

- role of hydrogen bonding in reduced sensitivity, importance of non-additive inter/intramolecular interactions, decomposition mechanisms

PROJECT OVERVIEW - POSS

Polyhedral oligomeric silsesquioxanes -- next generation plastics

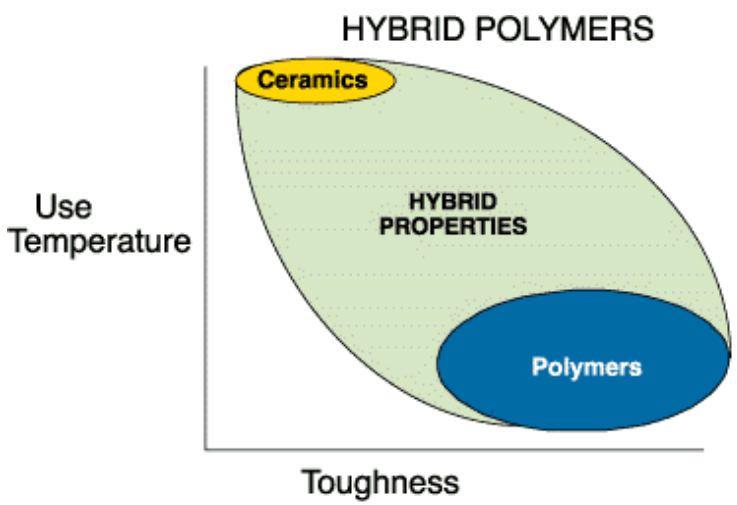




As Additives
Heat/abrasion resistant paints and coatings
Mechanical property/viscosity/thermal modifiers
Crosslinking agents
Fire retardants

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



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

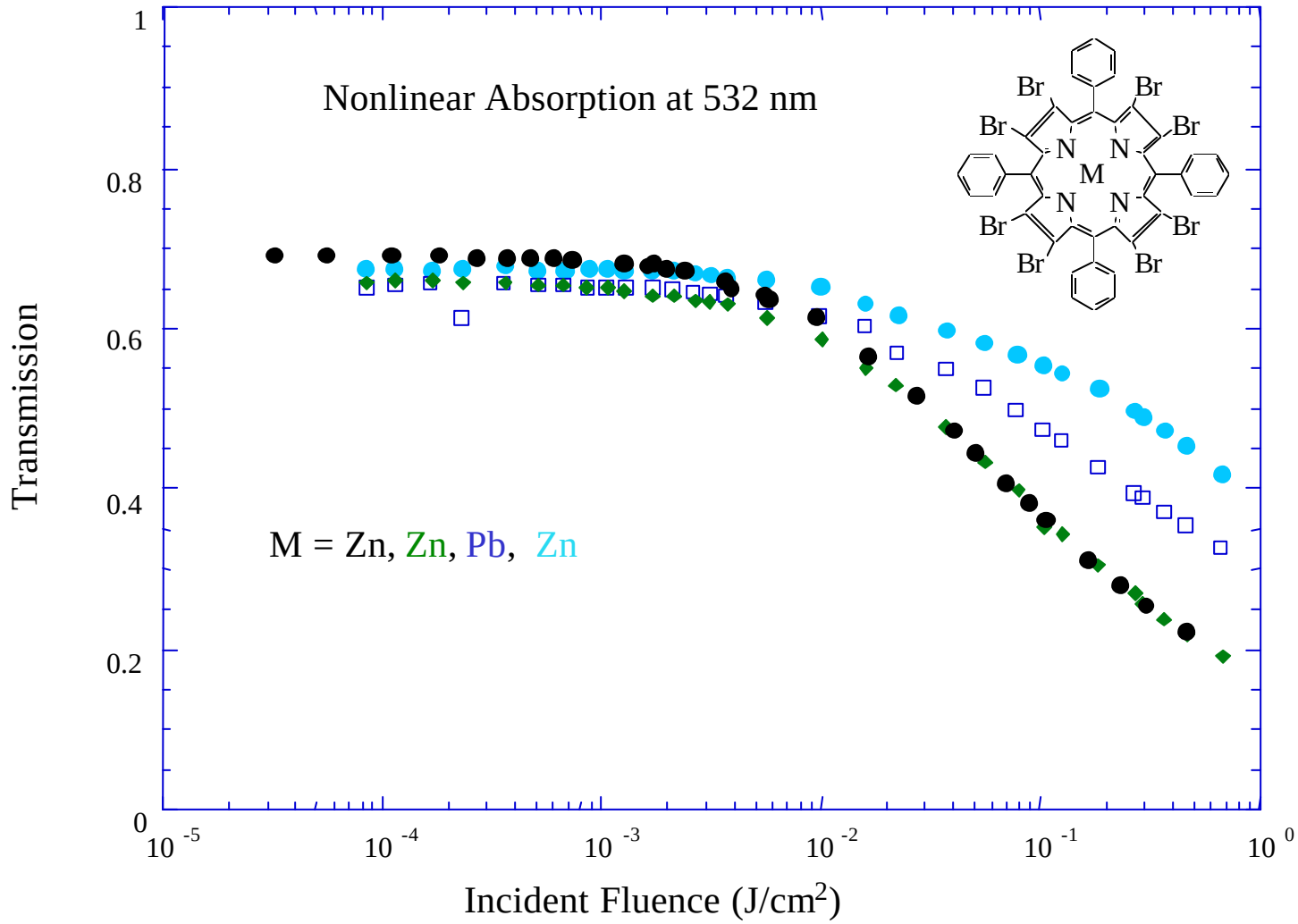
2. Potential applications as molecular "sieves"

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

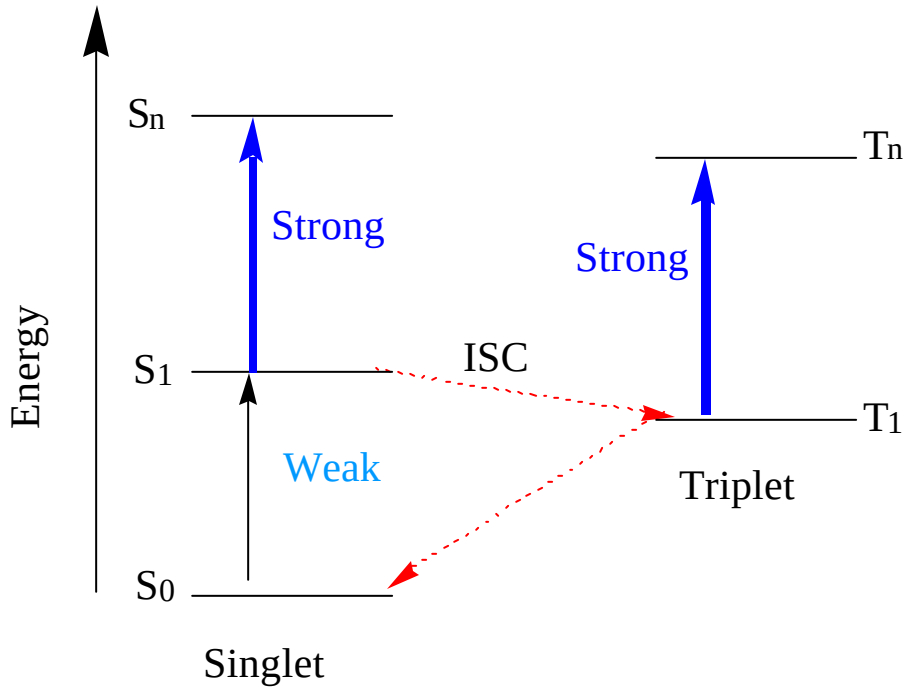
Non-linear optical materials for laser-hardened applications



PROJECT OVERVIEW - NLO

Technical issues being addressed using CCM

1. Mechanism of reverse saturable absorption (RSA)



Five-level model for nonlinear absorption

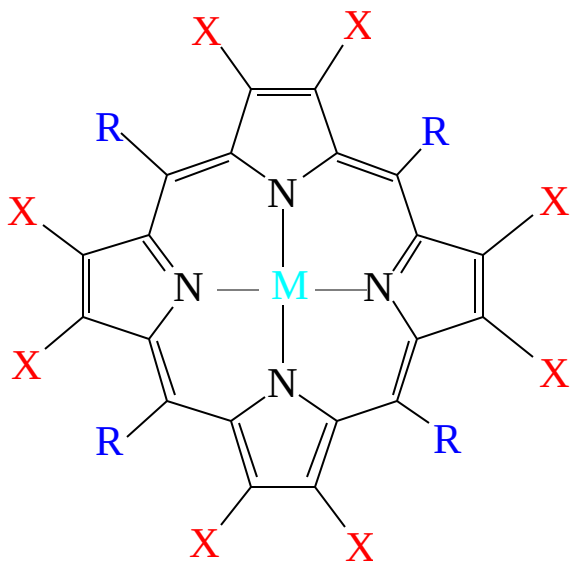
Key Components of RSA

- **Ground state spectra (linear response)**
- **Singlet-triplet splittings (ISC, phosphorescence)**
- **Ionization potential (photoionization)**
- **Excited triplet spectra (NLA)**

PROJECT OVERVIEW - NLO

Technical issues being addressed using CCM

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



System				Property			
	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	f	E, C	E, C	E, C	E, C
ZnTPP	Zn	H	f	E, C	E, C	E, C	E, C
$ZnTPPBr_8$	Zn	Br	f	C	E, C	E, C	E, C

IP = Ionization Potential, S_0 -S_n = Ground State Spectrum,
S_0 -T_1 = Singlet-Triplet Gap T_1 -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:

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

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., "clampled nuclei") approximation -- NOE method treats specified nuclei at QM level.

Nuclear-Electronic Hamiltonian

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

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

	RHF	ROHF	UHF	GVB	MCSCF
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
MP2 gradient	cdp	-	-	-	-
CI energy	cdp	cdp	-	cdp	cdp
CI gradient	cd	-	-	-	-

c = conventional disk storage of AO integrals

d = direct evaluation of AO integrals

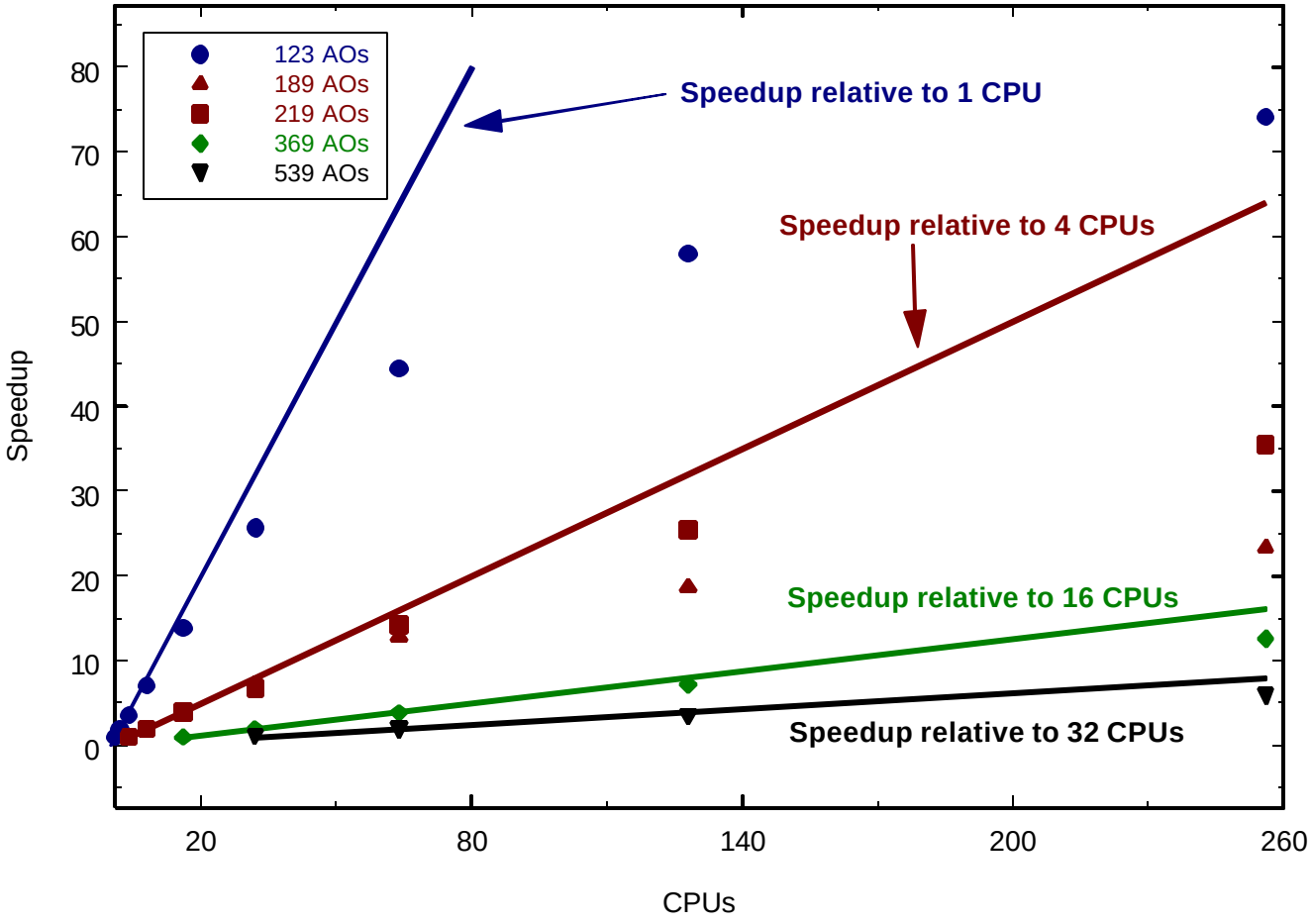
p = run in parallel

THEORETICAL METHODS

Ab initio electronic structure theory

MP2 Gradient Scalability Test

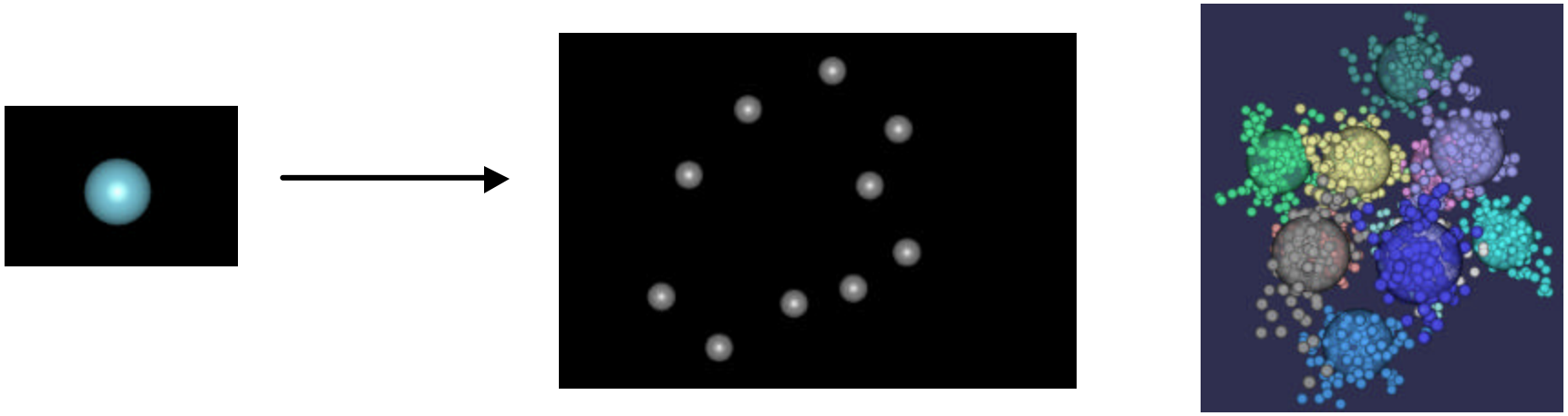
Silicocene molecule, Si(C5H5)2



THEORETICAL METHODS

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

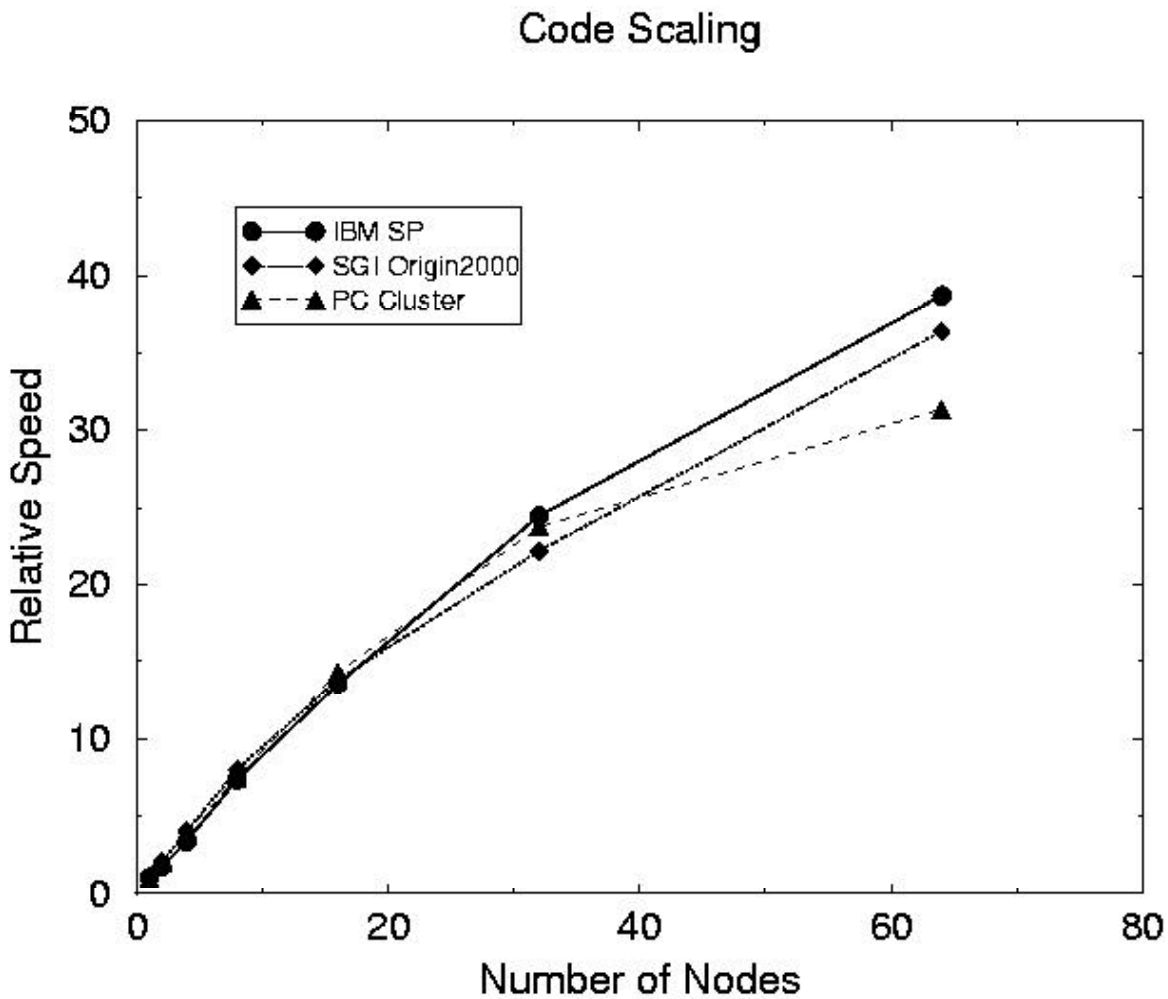
Simulation methods based on path integral techniques for mapping quantum particles onto "polymer ring" of classical quasiparticles:



Each "real" particle is replaced by N (50<N<500) quasiparticles; classical dynamics done on collection of quasiparticles => natural, efficient parallelism.

THEORETICAL METHODS

Path Integral Molecular Dynamics & Centroid Molecular Dynamics

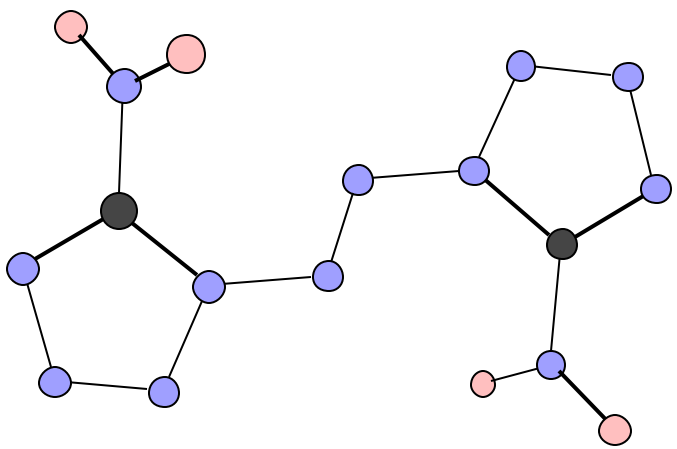


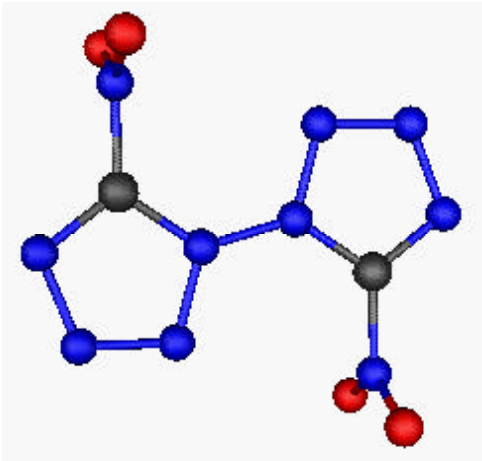
RESULTS - HEDM

High-nitrogen/polynitrogen compounds

Predicted ΔH_f = 457 kcal/mol, I_{sp} = 240 sec

(I_{sp} for hydrazine = 233 sec)





+ N_2

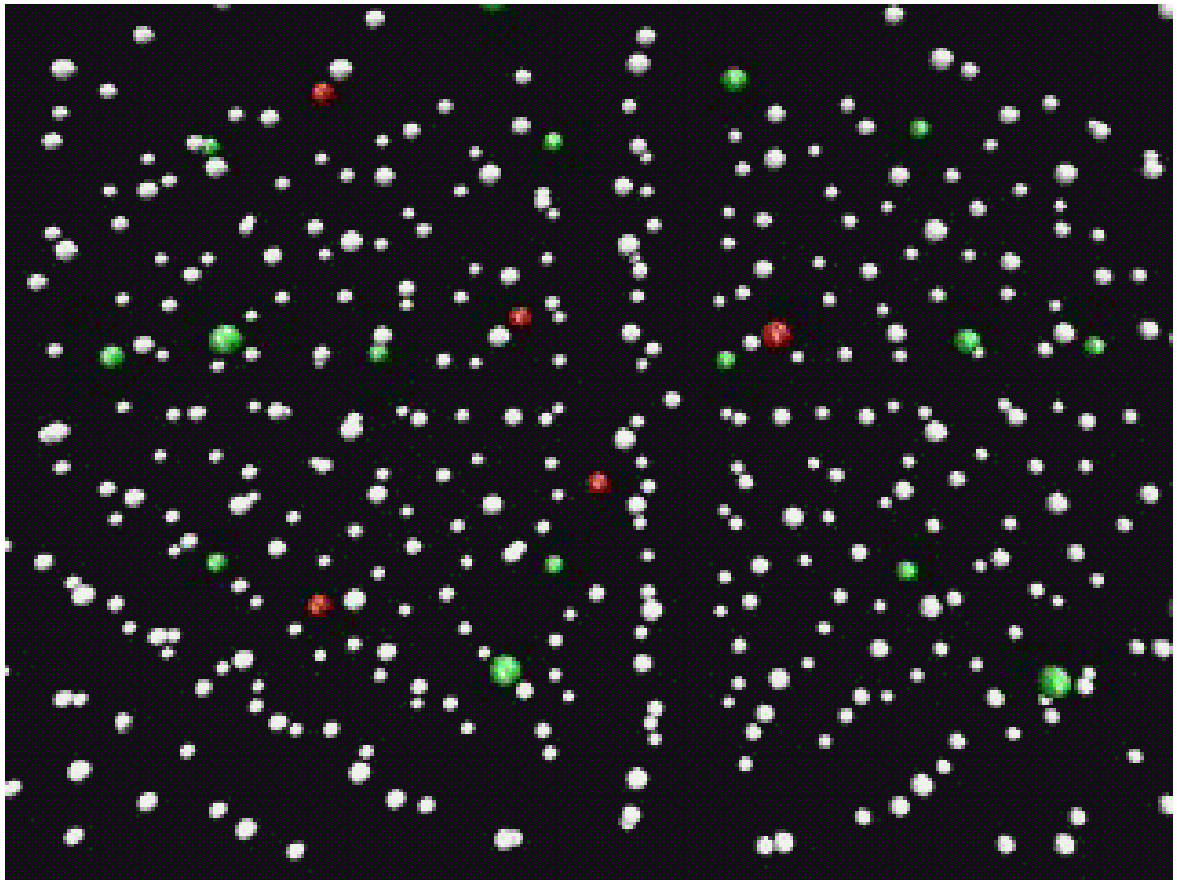
Predicted ΔH_r = -60 kcal/mol, calculation of reaction barrier underway

Computational requirements: ~60,000 node-hrs, ERDC T3E, 64 GB memory

RESULTS - HEDM

Atom-doped solid hydrogen

6.25% B atoms in solid *para*-H_2



Previous key results

1. In sH_2, 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:

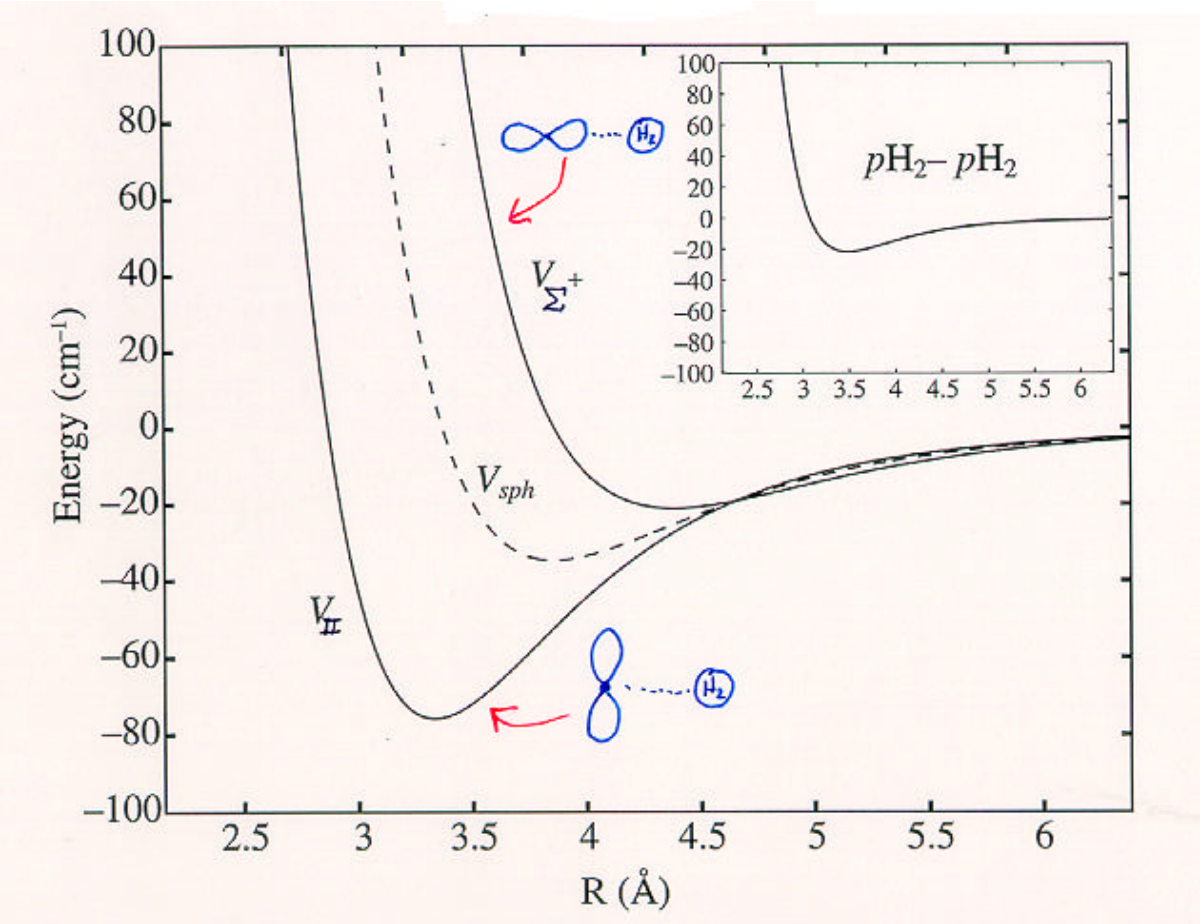
~50,000 CPU-hrs, MHPCC IBM SP

S. Jang, S. Jang, and G.A. Voth, J. Phys. Chem. A, 103, 9512(1999)

RESULTS - HEDM

Atom-doped solid hydrogen

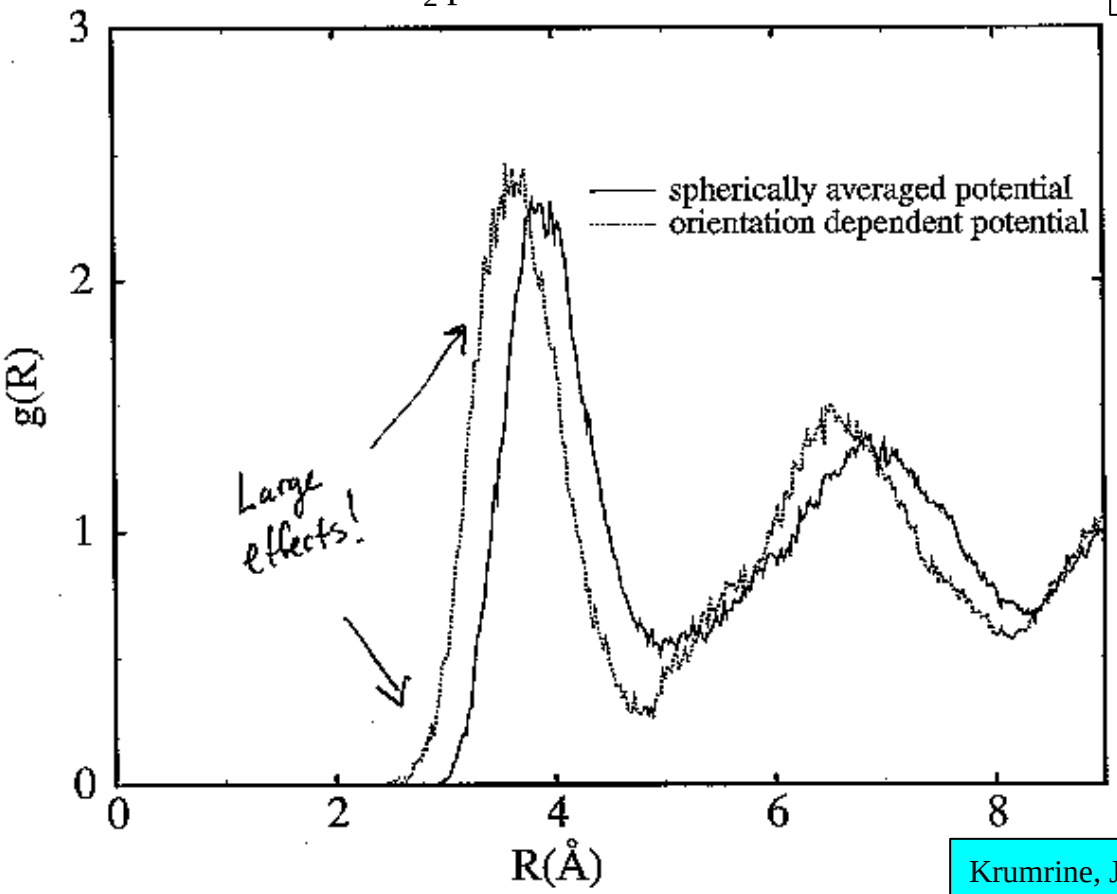
How important is the orientational dependence of B-H_2 interactions in B/sH_2?



RESULTS - HEDM

Atom-doped solid hydrogen

B-H_2 pair correlation function



B-H_2 interaction energies (cm^{-1})

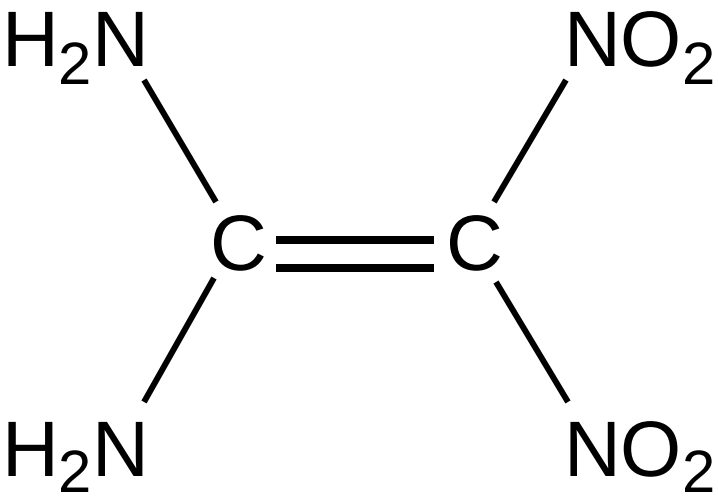
Site	$\langle V_{B-H2} \rangle$
1-atom substitution	-546.72 (o.d.) -443.32 (sph.)
1-atom sub. + vacancy	-538.49 (o.d.) -439.88 (sph.)
surface	-375.32 (o.d.) -261.64 (sph.)

The bottom line: more accurate potentials predict greater stability of B atoms in solid H_2!

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

RESULTS - HEDM

FOX-7 (1,1-diamino-2,2-dinitroethylene)



I_{sp} = 254 sec (calculated)
ΔH_f = -9.5 kcal/mol (G2(MP2))

Advantages:

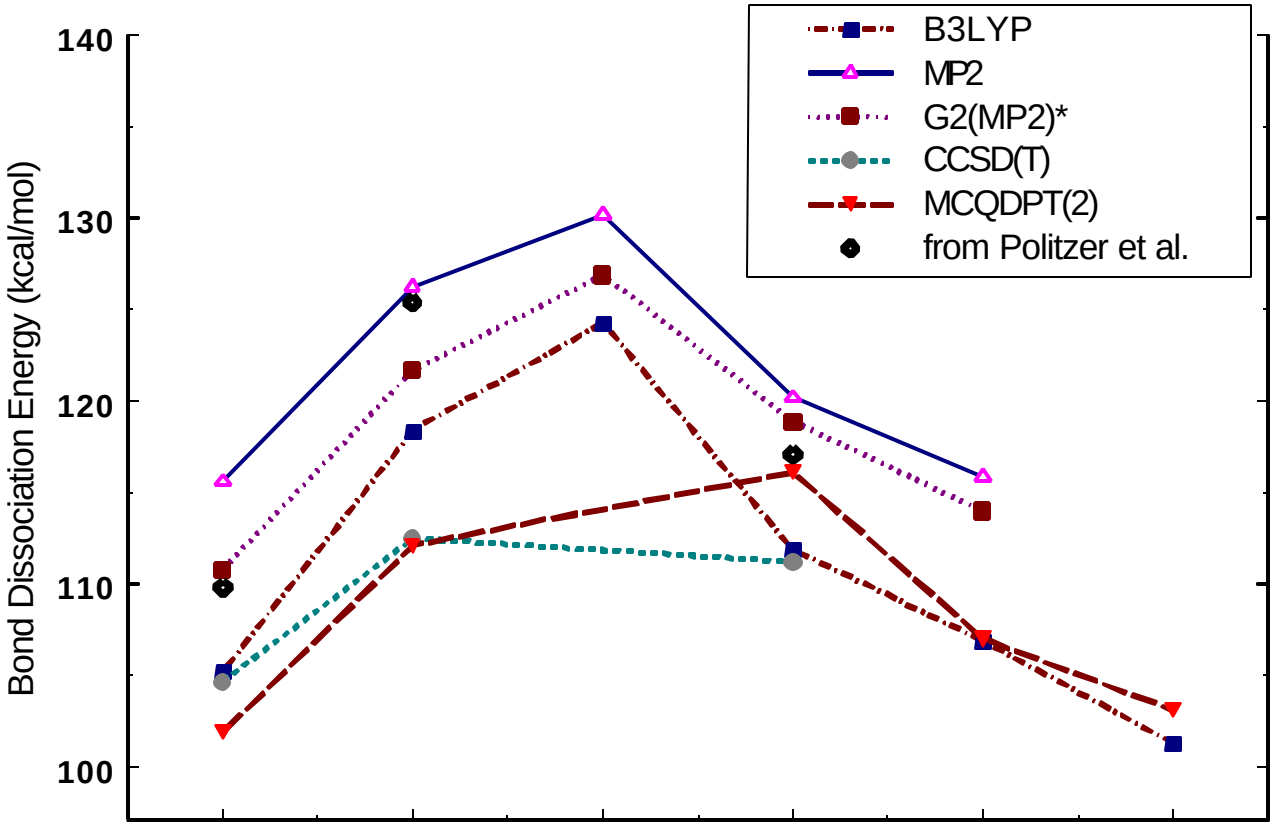
- Chemically balanced wrt decomposition products ($2CO + 2H_2O + 2N_2$)

- Lower impact/shock sensitivity than other $C_nH_{2n}O_{2n}N_{2n}$ compounds (e.g., RDX and HMX).

D.C. Sorescu, J.A. Boatz, D.L. Thompson, J. Phys. Chem. A, 105, 5010(2001).

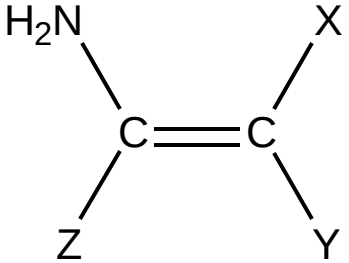
RESULTS - HEDM

Development of a solid-state force field: calibration of theoretical methods for computing bond dissociation energies



X=	H	NO_2	NO_2	NO_2	NO_2	H
Y=	H	H	NO_2	NO_2	H	H
Z=	H	H	H	NH_2	NH_2	NH_2

HPC Requirements: 2 CPU-months, ARL SV-1, 1.3 GW memory, 190 GB disk



RESULTS - POSS

Mechanism of formation

Key steps

1. Hydrolysis of $RSiX_3$ (R=H,CH_3,t-butyl,etc.; X=Cl)

   $RSiCl_3 + H_2O \rightarrow RSiCl_2OH + HCl$

   $RSiCl_2OH + H_2O \rightarrow RSiCl(OH)_2 + HCl$

   $RSiCl(OH)_2 + H_2O \rightarrow RSi(OH)_3$

2. Condensation of $RSi(OH)_3$ to disiloxane

   $2\ RSi(OH)_3 \rightarrow R(OH)_2SiOSi(OH)_2R + H_2O$

3. Condensation of disiloxane to D_3,D_4

   $RSi(OH)_3 + R(OH)_2SiOSi(OH)_2R \rightarrow D_3 + 2H_2O$

   [2+2]: $2R(OH)_2SiOSi(OH)_2R \rightarrow D_4 + 2H_2O$

   [3+1]: $RSi(OH)_3 + R(OH)_2SiOSi(OH)_2R \rightarrow D_4 + 2H_2O$

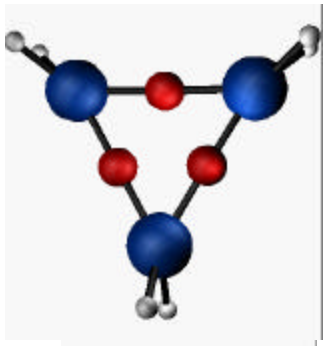
   Ring Expansion: $RSi(OH)_3 + D_3 \rightarrow D_4 + H_2O$

4. Condensation of D_3, D_4 to POSS (in progress)

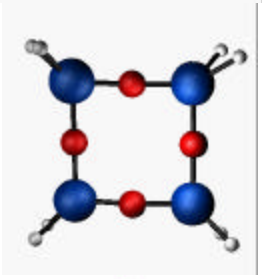
   $2D_4 \rightarrow T_8 + 4H_2O$

   ....

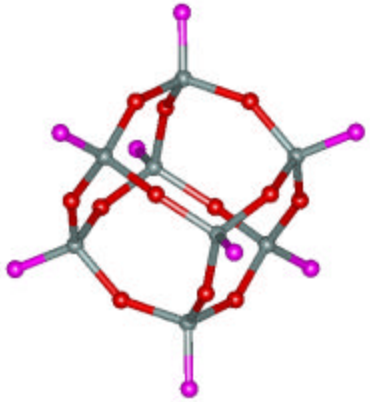
D3



D4



T8



RESULTS - POSS

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

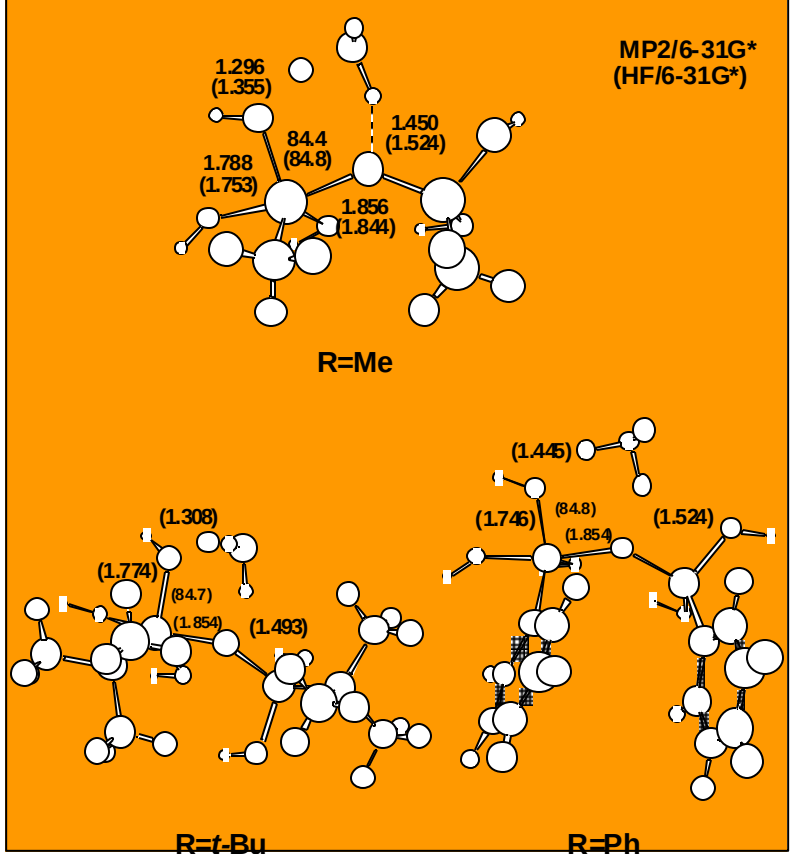
$RSi(OH)_3 + RSi(OH)_3 \rightarrow R(OH)_2SiOSi(OH)_2R + H_2O$

R	Energy barrier (kcal/mol)	
	HF/6-31G*	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.

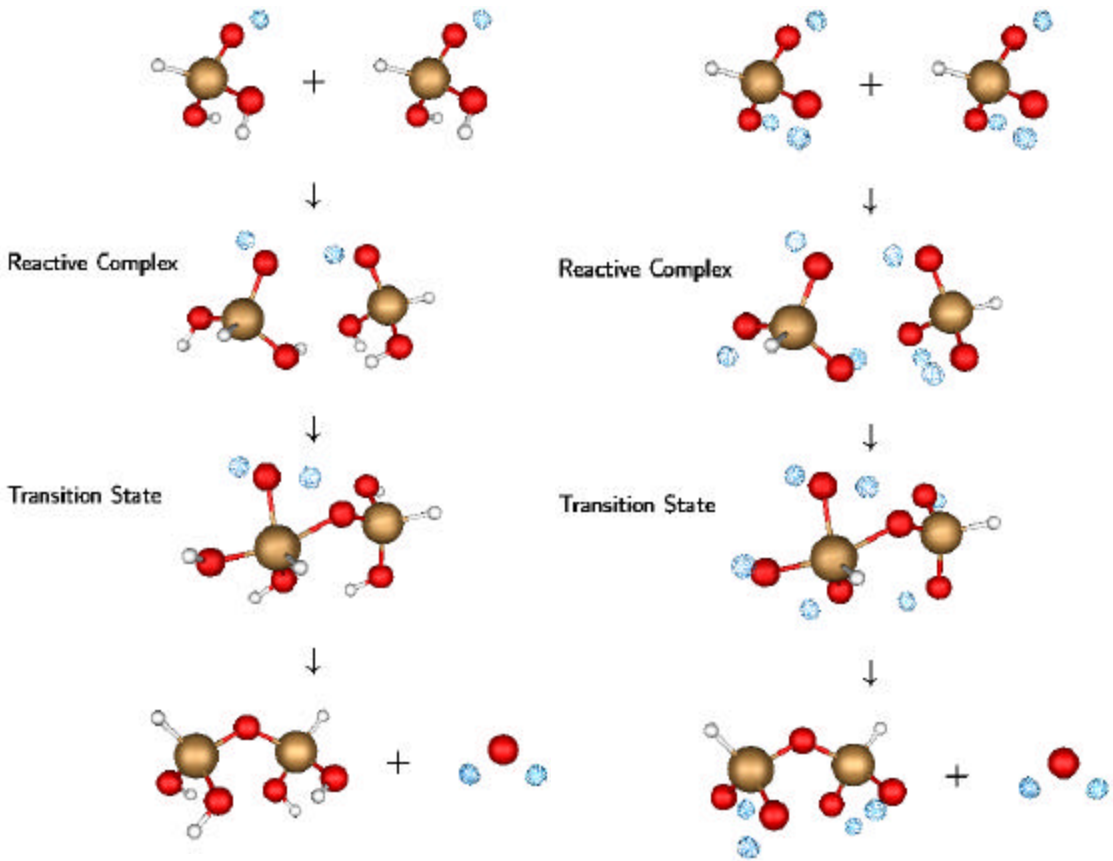
Kudo, T., Gordon, M.S. J. Am. Chem. Soc., 120, 11432 (1998)
Kudo, T., Gordon, M.S. J. Phys. Chem. A, 104, 4058 (2000)

TS for the condensation of $RSi(OH)_3$ catalyzed by a water



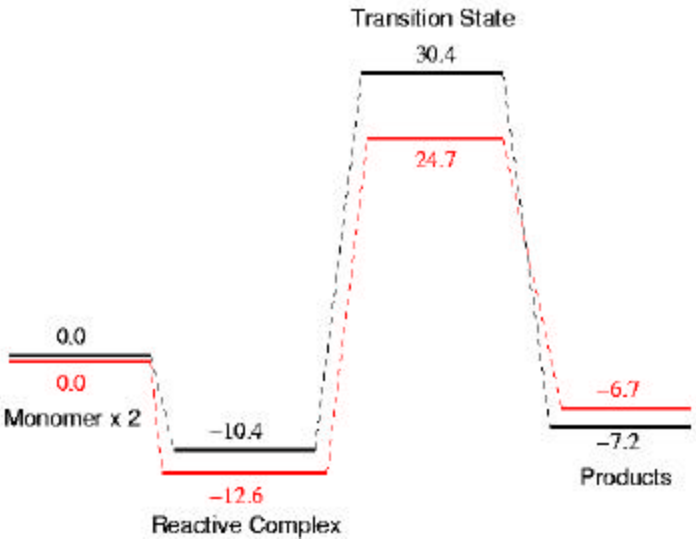
RESULTS - POSS

Nuclear quantum effects in proton transfer reactions



Level	Monomer × 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



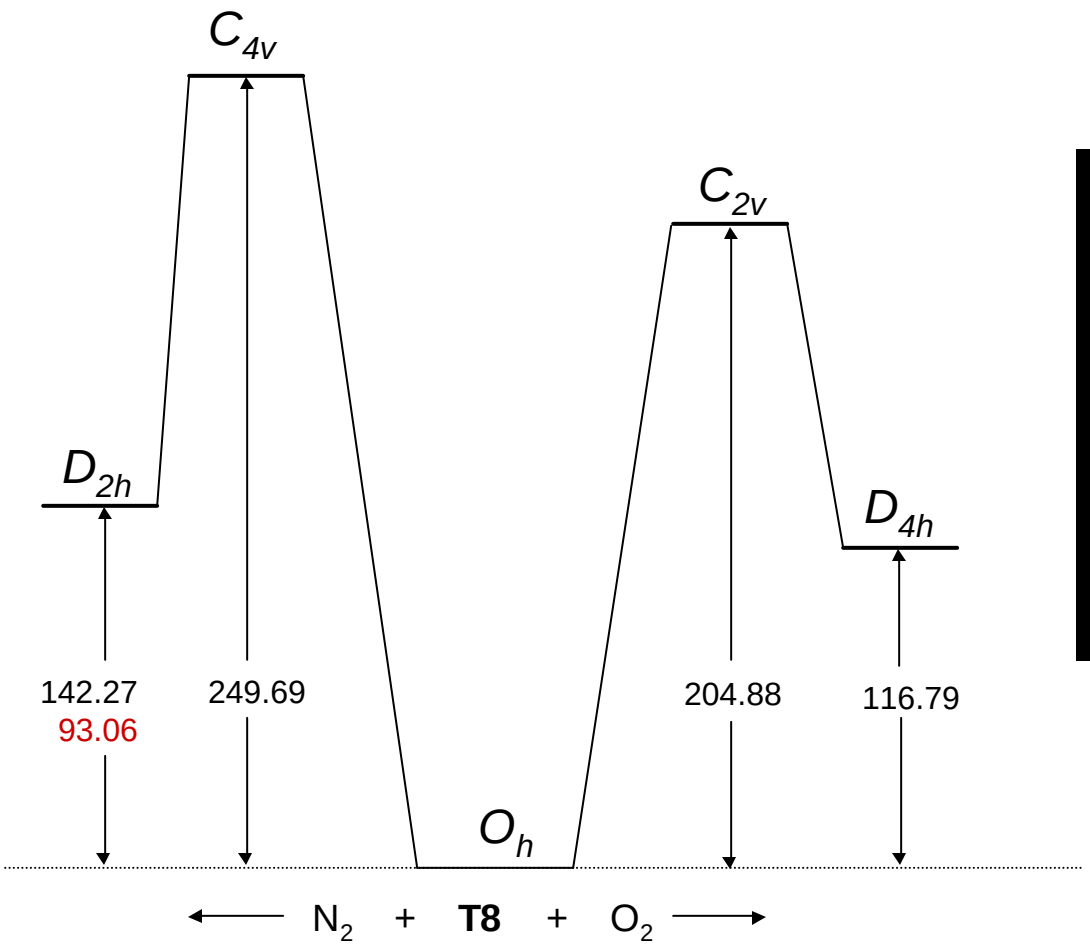
Hammes-Schiffer, S.: J. Phys. Chem. A 102 (1998), 10443

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

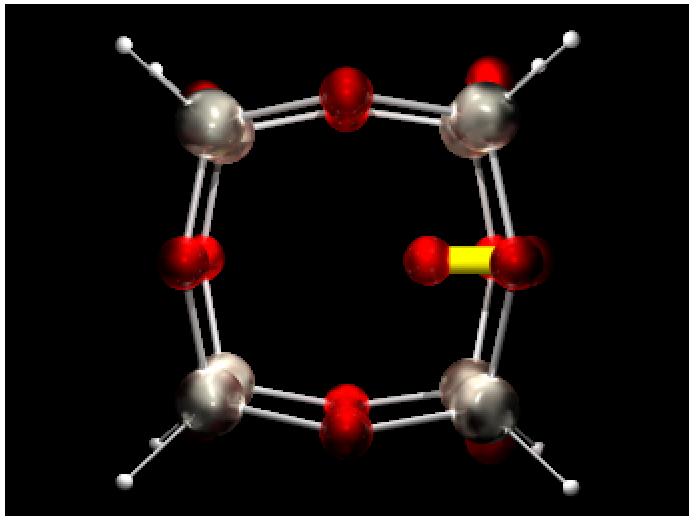
Webb,S.P. and Hammes-Schiffer, S.: J. Chem. Phys. 113 (2000), 5214

RESULTS - POSS

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, AHPCRC 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[a]
Zinc Porphyrin (1^3B_{1u})	1.65	0.07	1.72[b]
Tetraphenylporphyrin (1^3B_1)	1.31	0.14	1.45[c]
Zinc Tetraphenylporphyrin(1^3B_1)	1.53	0.06	1.59[d]
Zinc Phthalocyanine (1^3B_{2u})	1.05	0.08	1.13[e]
Zinc Tetrabenzporphyrin (1^3B_{1u})	1.41	0.16	1.57[f]
Phthalocyanine (1^3B_{1u})	1.18	0.06	1.24[g]
Mean Error		0.10	

[a]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) [b]Gradyushko, Tsvirko, *Opt. Spectrosc.* 1971, *31*, 291.(EPA at 77 K) [c]Gouterman, Khalil, *J. Mol. Spectrosc.* 1974, *53*, 88. (EPA at 77 K) [d]Walters et al., *J. Phys. Chem.* 1995, *99*, 1166.(1:1 mixture of ether to ethanol at 77 K) [e]Vincett et al.,K. E. *J. Chem. Phys.* 1971, *55*, 4131. (1-chloronapthalene at 77 K) [f]Bajema, Gouterman, *J. Mol. Spectrosc.* 1971, *39*, 421 (octane at 77 K) [g]McVie et al., *J. Chem. Soc. Faraday Trans. II* 1978, *74*, 1870 (1-chloronapthalene at 77 K)

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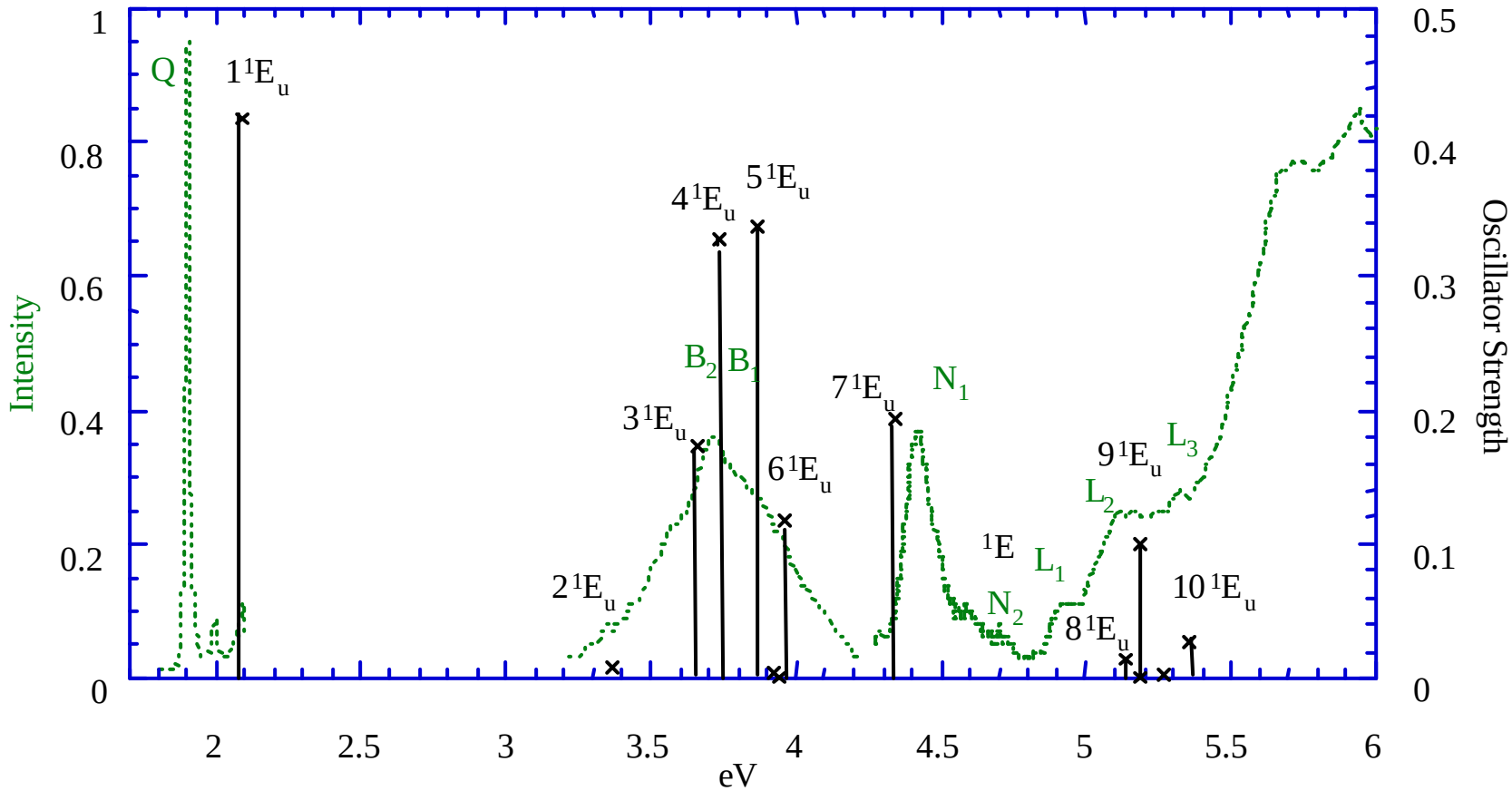
RESULTS - NLO

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.
- Inclusion of anisotropic interactions of B atoms in sH_2 predict greater stability than spherical interaction model.
- Extensive network of hydrogen bonds in FOX-7 may be responsible for lower shock, friction sensitivity relative to HMX, RDX.

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

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

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