

# Materials Modeling for Rocket Propulsion

OSC Workshop on Materials  
Modeling for National Security

16-17 May 2005

Jerry Boatz

Propellants Development Branch

Propulsion Directorate

Air Force Research Laboratory



This briefing contains information up to:

DISTRIBUTION A. Approved for public release; distribution unlimited.

# Report Documentation Page

*Form Approved  
OMB No. 0704-0188*

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE <b>APR 2005</b>	2. REPORT TYPE	3. DATES COVERED -	
4. TITLE AND SUBTITLE <b>Materials Modeling for Rocket Propulsion</b>		5a. CONTRACT NUMBER	
		5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) <b>Jerry Boatz</b>		5d. PROJECT NUMBER <b>2303</b>	
		5e. TASK NUMBER <b>0423</b>	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Air Force Research Laboratory (AFMC), AFRL/PRSP, 10 E. Saturn Blvd., Edwards AFB, CA, 93524-7680</b>		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)	
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>			
13. SUPPLEMENTARY NOTES			
14. ABSTRACT <b>N/A</b>			
15. SUBJECT TERMS			
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>	18. NUMBER OF PAGES <b>22</b>
			19a. NAME OF RESPONSIBLE PERSON



# Outline



## 1. Introduction

## 2. Technical challenges in propellant design

## 3. Modeling and Simulation (M&S) techniques & tools

- a) Quantum chemistry
- b) Molecular dynamics
- c) QSPR
- d) High Performance Computing (HPC)

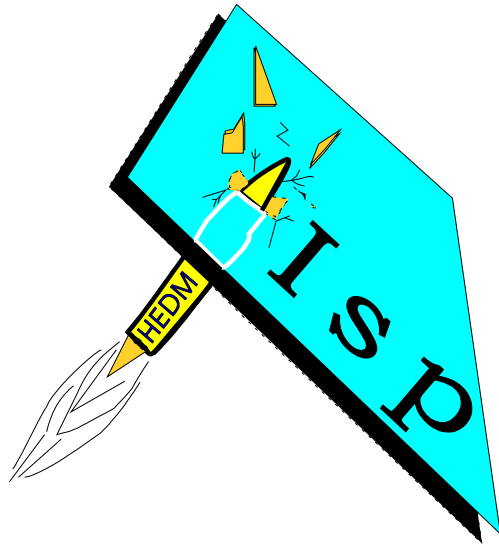
## 4. Examples

- a) Identification of suitable target compounds
- b) Determination of viable intermediates
- c) Confirmation of successful synthesis

## 5. Summary and Conclusions



# 1. What We Are Doing



*Breaking the performance barrier*

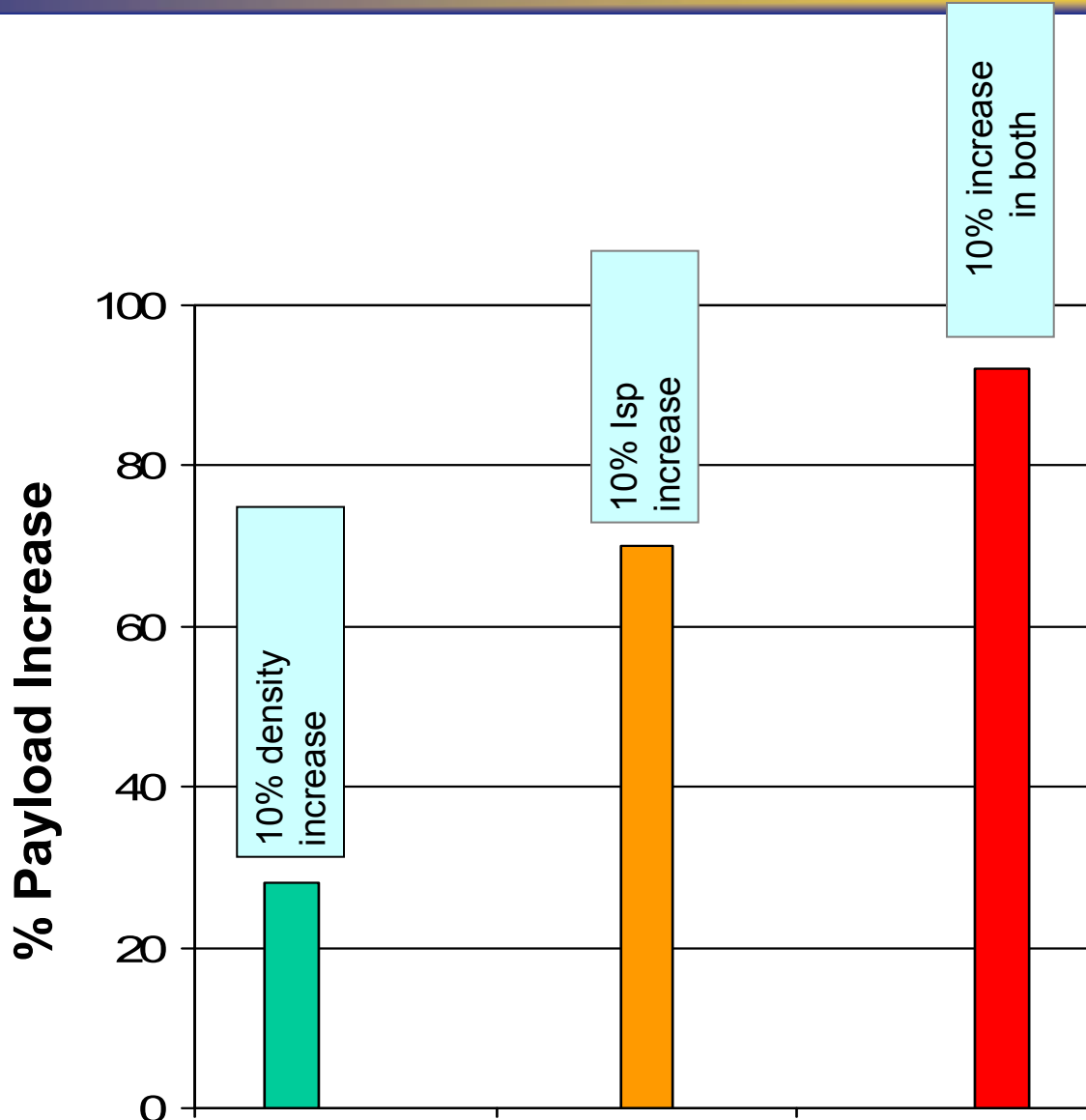
**Identifying and developing advanced chemical propellants for rocket propulsion applications**

- Isp is the major metric of a propellant's performance
- Density can also be a significant contributor





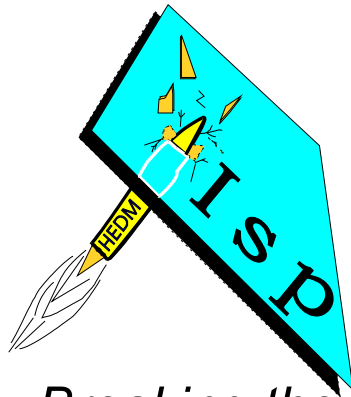
# 1. Why We Are Doing It





# 1. How We Do it

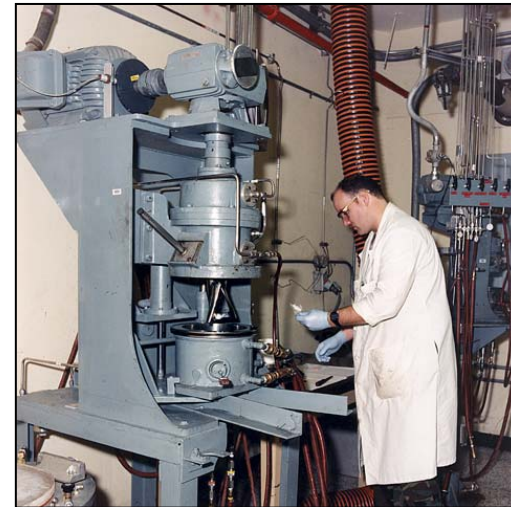
## High Energy Density Matter



*Breaking the performance barrier*

- Advanced solid ingredients
- Computational Chemistry
- Polynitrogen chemistry
- Ionic liquids
- Advanced hydrocarbon fuels
- Ignition studies

## Propellant Development



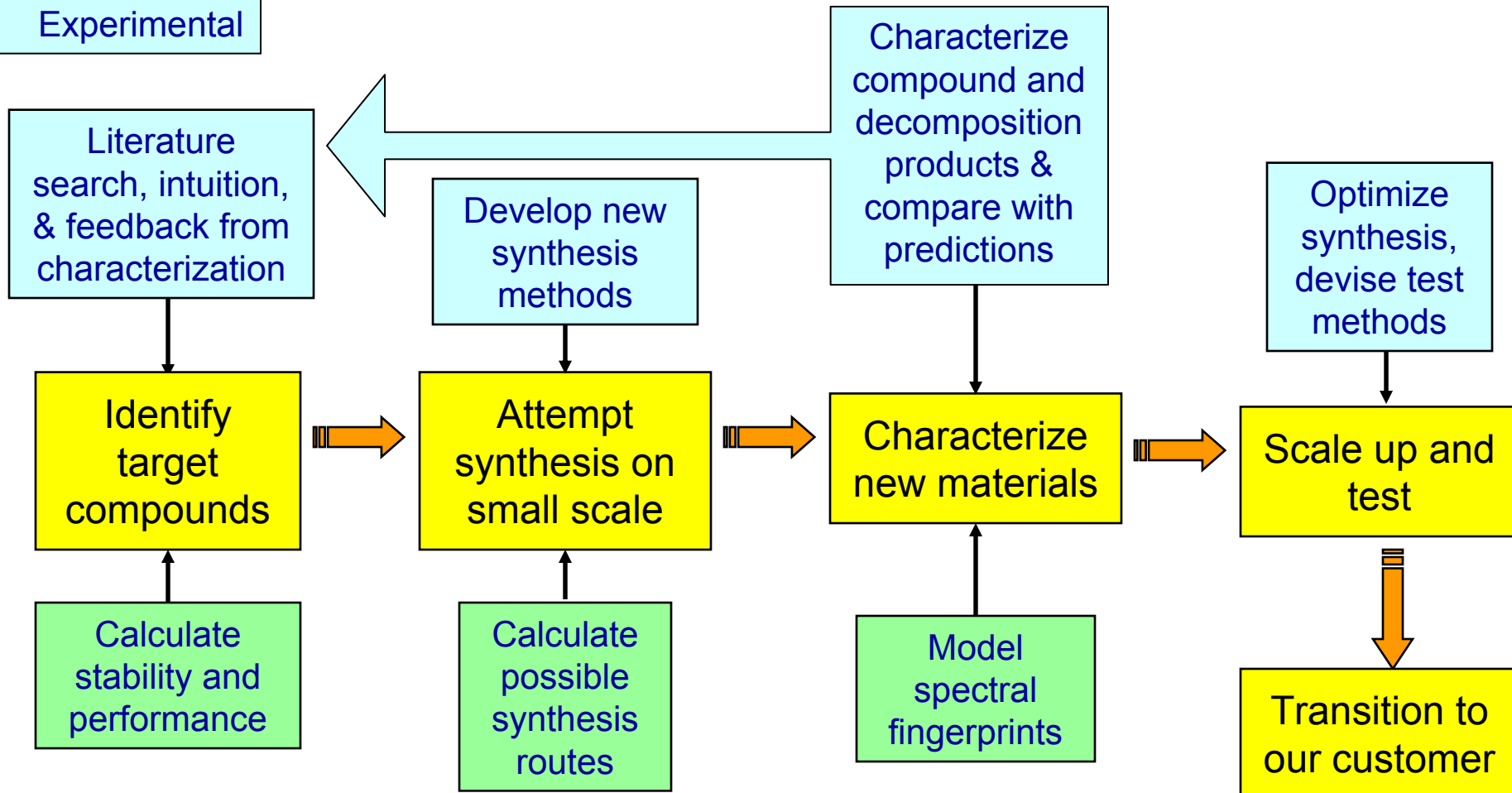
- Ingredient characterization
- Propellant characterization
- Ingredient scale up
- Propellant scale up
- Small scale hot fire propellant testing



# 1. Propellants Program General Approach

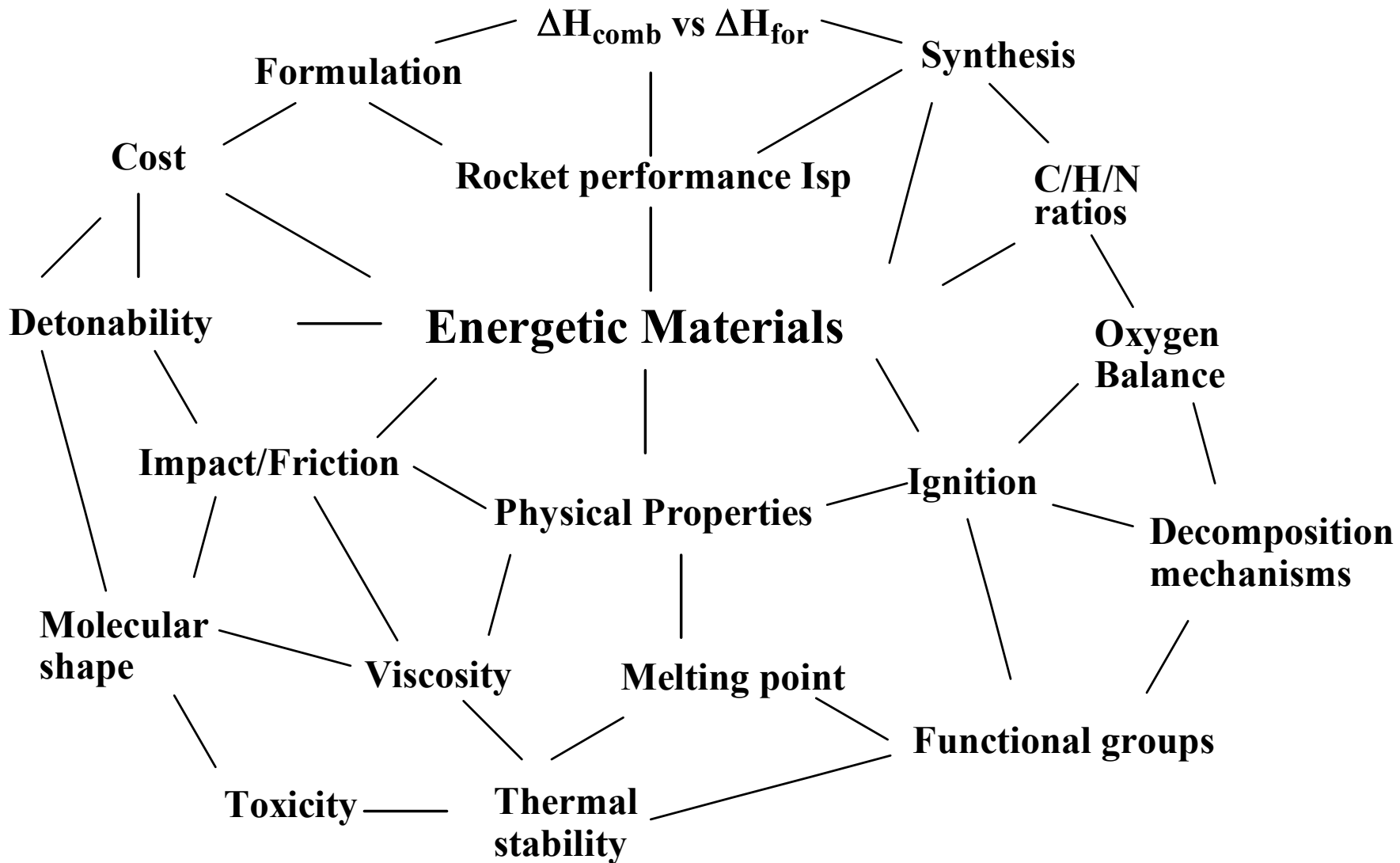
Employ a synergic blend of experimental (synthesis and physical) and computational techniques derived from the disciplines of chemistry and physics

Experimental





## 2. Challenges in Propellant Design





# 2. Challenges Addressed by M&S

**Stability**

**Energy Content**

**Reactivity**

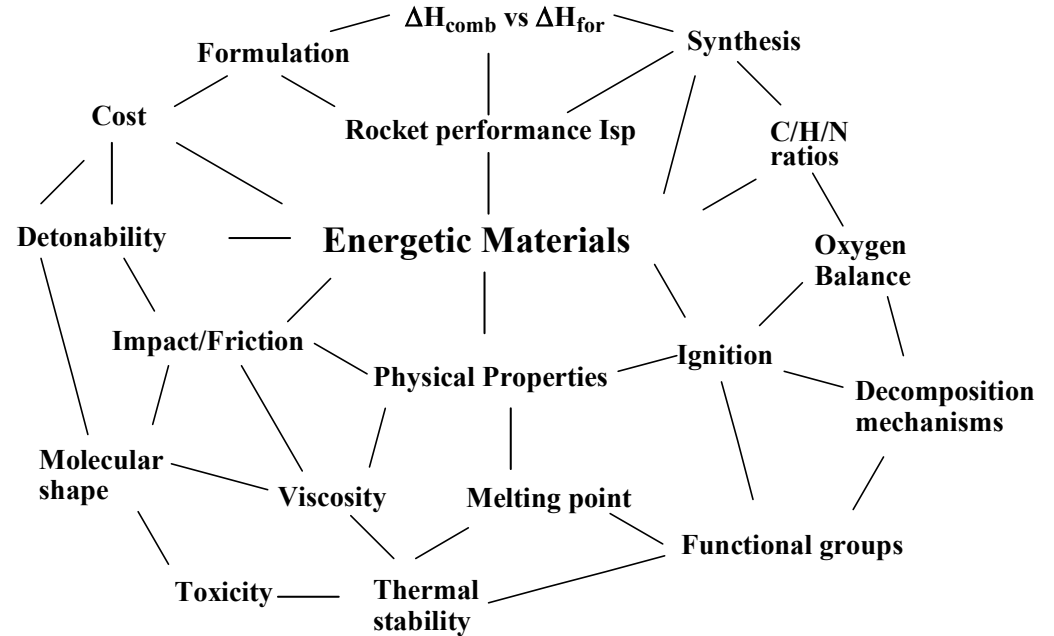
Synthesis  
Ignition  
Combustion  
Decomposition

**Bulk properties**

Melting points  
Densities  
Transport properties (e.g., thermal conductivity)

**Sensitivity (impact/friction/shock)**

**Toxicity**





### 3. M&S of New Chemical Propellants: Quantum Chemistry



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

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

**Is a proposed propellant molecule/energetic material stable?**

Structure optimization, verification as local minimum

**What is its energy content?**

Heat of formation

**How may it be synthesized? How will it react/decompose/combust?**

Reaction pathways

**How will we know if we've synthesized it?**

Vibrational spectra (IR, Raman, isotopic shifts)

NMR chemical shifts

Electronic spectra



### 3. *M&S of New Chemical Propellants: Molecular Dynamics*



Classical Equations of motion solved to simulate and predict various properties

$$\vec{F} = m\vec{a}$$

#### **Bulk properties**

Phase transitions (esp. melting points), densities, transport properties

#### **Processes affecting sensitivity**

Shock wave propagation vs. dissipation, energy transfer



### 3. *M&S of New Chemical Propellants: QSPR*



Derivation of empirical expressions relating molecular descriptors to key properties

**Bulk Properties**

**Sensitivity**

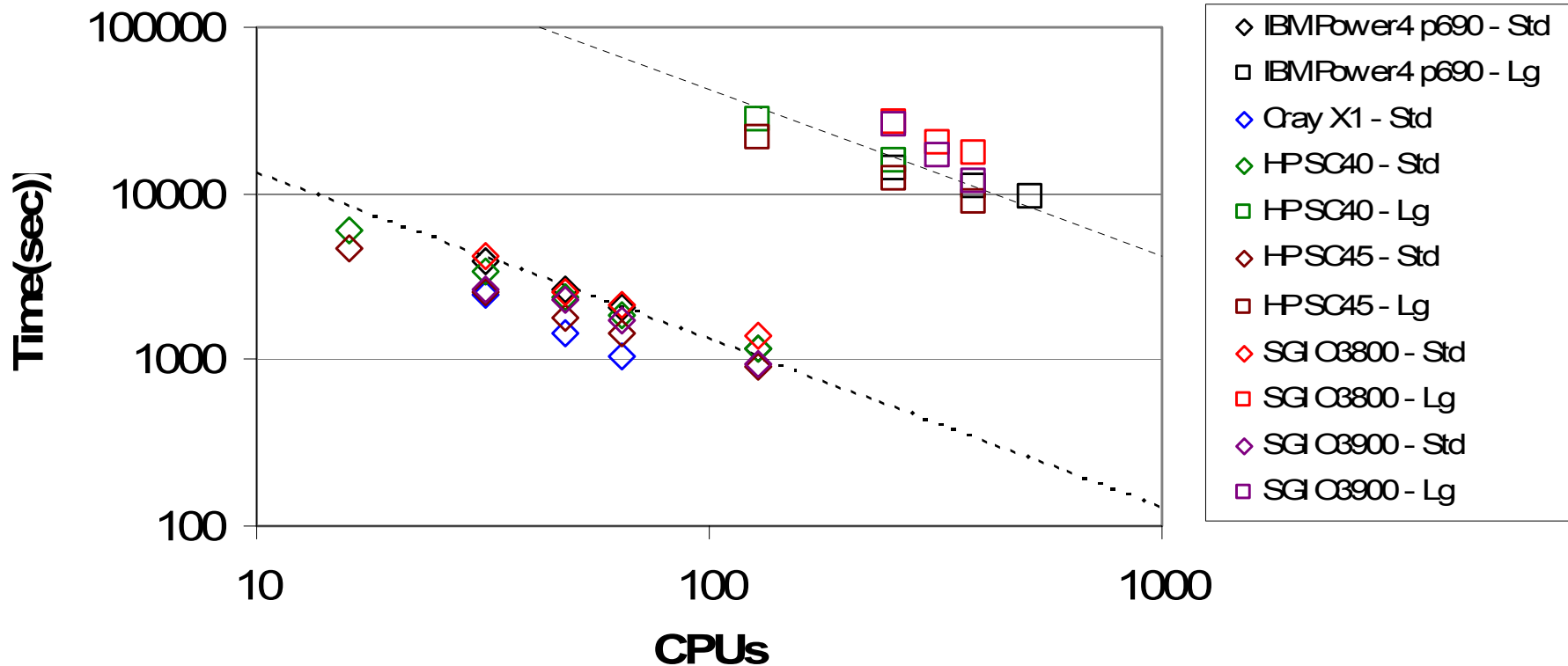
**Toxicity**



# 3. M&S of New Chemical Propellants: High Performance Computing



## GAMMESS Benchmark Times





### 3. HPC Tools



Software: A variety of computer programs are used to perform the quantum chemical calculations, including:

- **GAMESS** (General Atomical and Molecular Electronic Structure System), from Iowa State University (Mark Gordon et al.)
- **ACES II** (Advanced Concepts in Electronic Structure), from University of Florida (Rod Bartlett et al.)
- **GAUSSIAN 98**, from Gaussian, Inc. (John Pople et al.)
- **MOLPRO 98**, from University of Birmingham (UK)

Hardware: A variety of scalable computing systems (IBM SP/Px, Cray T3E, SGI Origin, Linux clusters, etc.) at the DoD HPC centers, plus local computing resources.



## 4. *Examples*



**The AFRL-Edwards (PRSP) theory/computational group supports several in-house experimental programs:**

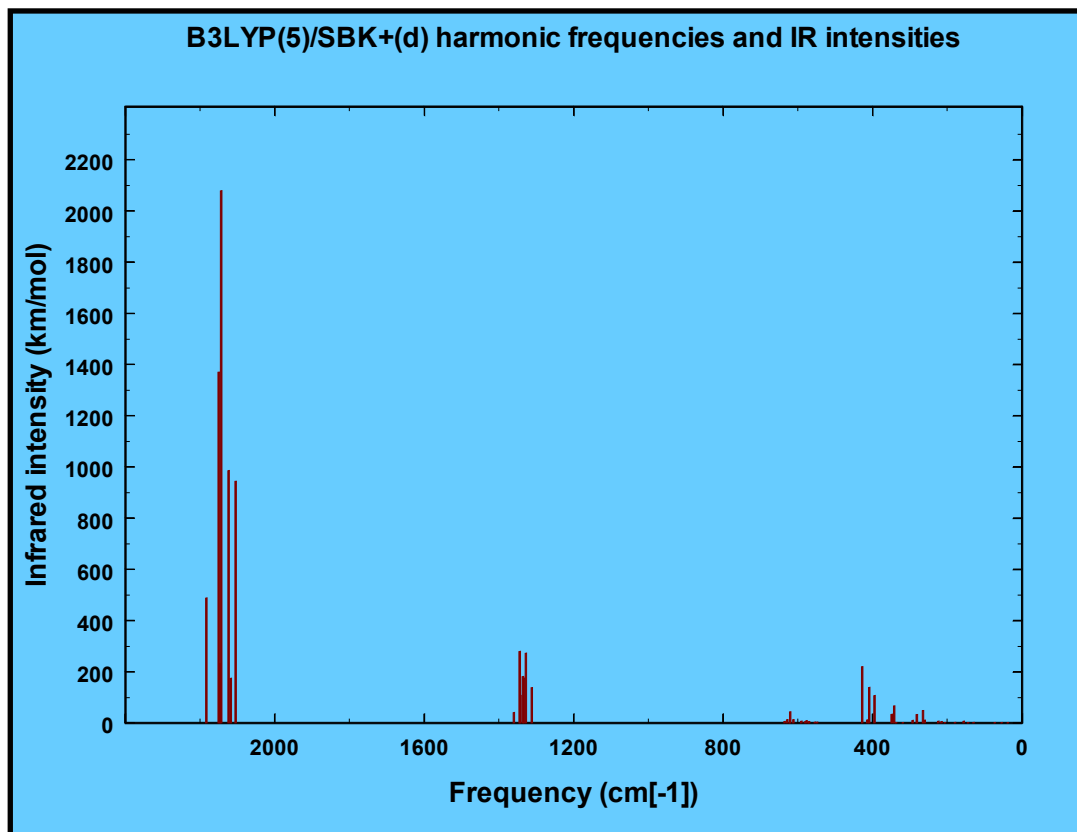
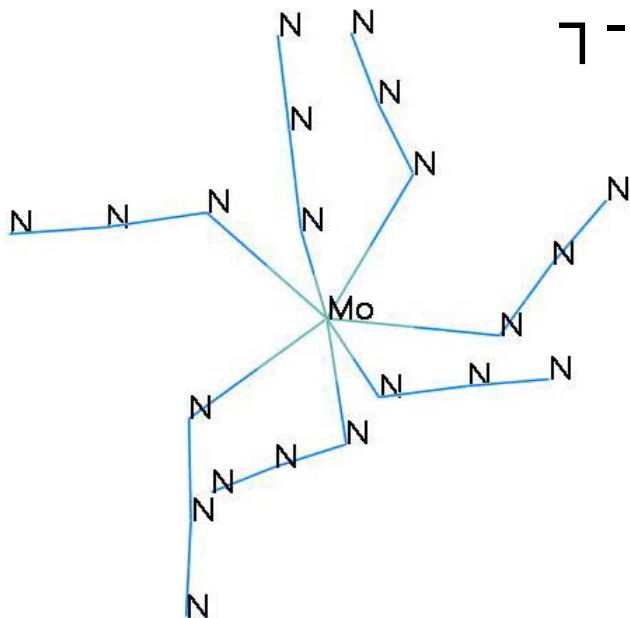
- ▶ **a) Polynitrogen/high nitrogen chemistry**
- ▶ **b) Energetic ionic liquids**
- ▶ **b) Ionic liquids ignition/combustion**
- ▶ **c) Energetic hydrocarbons**
- ▶ **d) Energetic solid ingredients**



# 4. New Polynitrogens/High Nitrogen Compounds: Identifying Intermediates



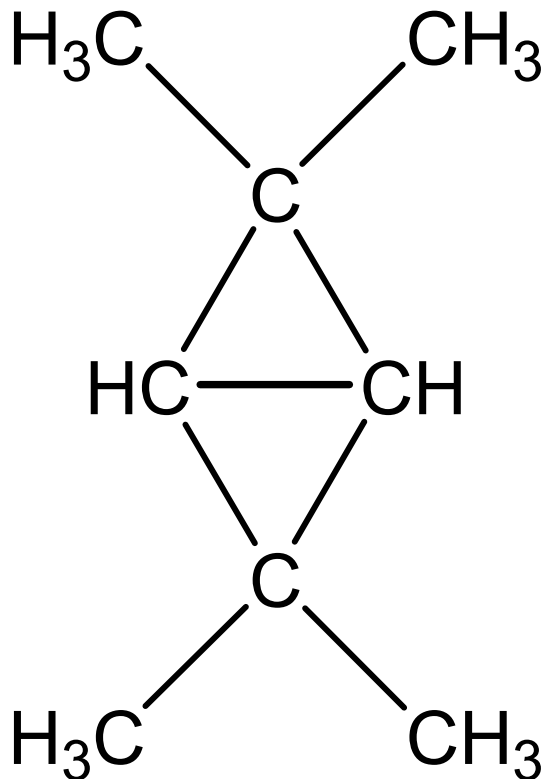
**Role of theory and computation:** We calculate the structures, infrared and Raman vibrational spectra, and isotopic vibrational shifts.





# 4. Energetic Hydrocarbons: Identifying Target Compounds

**Role of theory and computation:** We calculate the structures, vibrational spectra, heats of formation, and Isp of new hydrocarbons



2,2,4,4-tetramethylbicyclo[1.1.0]butane

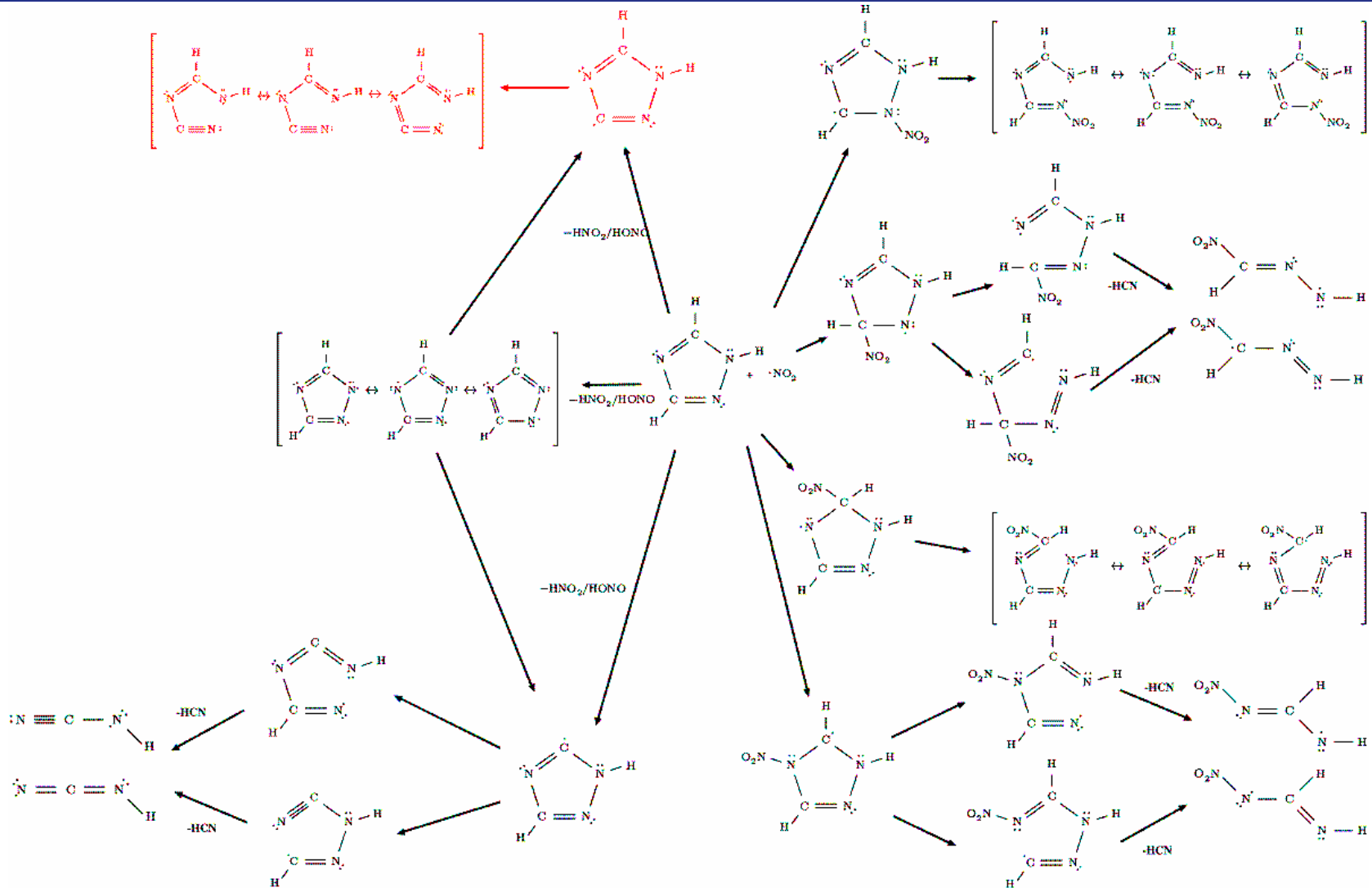
## Potential payoffs of advanced hydrocarbons

- Enabling new missions – up to 30% more payload on launch vehicles
- Cutting payload-to-orbit costs – 15% reduction for current expendable rockets; 90% reduction if incorporated into next-generation reusables

$$\underline{\Delta H_f} = 0.285 \text{ kcal/g}$$



# 4. Hypergolic Ignition Modeling



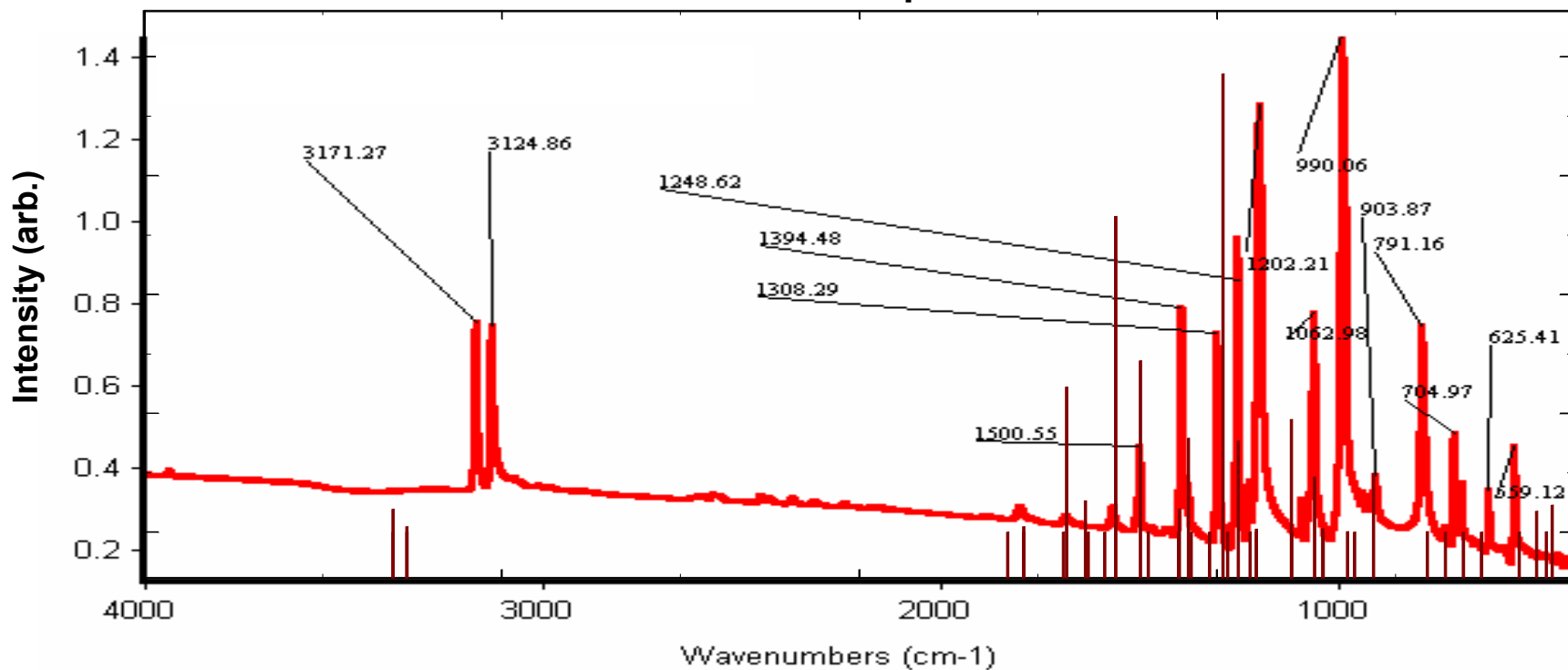


# 4. Energetic Solid Ingredients: Confirmation of Successful Synthesis



**Role of theory and computation:** We calculate the structures, infrared and Raman vibrational spectra, and isotopic vibrational shifts.

Comparison of calculated (B3LYP(5)/6-311G(d,p)) and experimental infrared vibrational spectrum.





## 5. Collaborators



Dr. Jeff Mills (AFRL/PRSP) – ignition studies, QSPR, ionic liquids, hydrocarbons, ....

### ▪ Extramural collaborations

Spectral Theory: Prof. Peter Langhoff (**San Diego Supercomputing Center**), Prof. R.J. Hinde (**Univ. of Tennessee-Knoxville**), Dr. Jeff Sheehy (**NASA MSFC**).

Solid Ingredients: Prof. Don Thompson (**University of Missouri-Columbia**), Dr. Dan Sorescu (**USDOE National Renewable Energy Laboratory**)

Ionic Liquids: Prof. Mark Gordon (**Iowa State University**), Prof. Greg Voth (**Univ. of Utah**), Prof. Sharon Hammes-Schiffer (**Univ. of Penn.**), Dr. Ruth Pachter (**AFRL/ML**).

Hydrocarbons: Dr. Mike Zehe (**NASA GRC**)



## 5. Summary



### **M&S plays a central role in propellant development**

- used to identify target compounds, characterize synthesis routes and viable intermediates, verify successful synthesis
- prediction of bulk properties, including phase transitions, densities, thermal conductivities
- QSPR is useful tool for characterizing bulk properties, including toxicities

### **Future directions(?)**

- Atomic-level modeling of processes affecting sensitivities (esp. for ionic materials)
- Models for aging and surveillance in support of strategic sustainment



## 6. Backup Slides



# 3. Parallel Algorithms in GAMESS



**GAMESS is one of three codes ported to scalable hardware platforms as part of PRSP's CHSSI project.**

Calc. type\Wavefunction type	RHF	ROHF	UHF	GVB	MCSCF
Energy	CDP	CDP	CDP	CDP	CDP●
Gradient	CDP	CDP	CDP	CDP	CDP●
Numerical Hessian	CDP	CDP	CDP	CDP	CDP●
Analytic Hessian	CDP	CDP	-	CDP	CDP
CI energy	CDP●	CDP●	n/a	CDP	CDP
CI gradient	CD	-	n/a	-	-
MP2 energy	CDP●	CDP●	CDP●	-	CP●
MP2 gradient	CDP●	-	CDP●	-	-
DFT Energy	CDP●	CDP●	CDP●	-	-
DFT Gradient	CDP●	CDP●	CDP●	-	-
CC Energy	CD	-	-	-	-