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Donald L. Thompson

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Oklahoma State University
Stillwater, OK 74078

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   This report describes the progress and accomplishments for the period June 1, 2002 to August 31, 2004 for the MURI grant "Accurate Theoretical Predictions of the Properties of Energetic Materials" (No. DAAD19-02-1-0176). This is a multi-university, comprehensive theoretical/computational research program to develop, validate, benchmark, and apply methods and models that will provide predictive capabilities for energetic materials. The thrust of the work is the development of atomic-level models and *ab initio* quantum chemistry methods that are generally applicable to the chemical decomposition of condensed-phase energetic materials under extreme conditions.

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DONALD L. THOMPSON
DEPARTMENT OF CHEMISTRY
OKLAHOMA STATE UNIVERSITY
STILLWATER, OKLAHOMA 74078

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Introduction

This report describes the progress and accomplishments for the period June 1, 2002 to August 31, 2004 for the MURI grant "Accurate Theoretical Predictions of the Properties of Energetic Materials" (No. DAAD19-02-1-0176). This is a multi-university, comprehensive theoretical/computational research program to develop, validate, benchmark, and apply methods and models that will provide predictive capabilities for energetic materials. The thrust of the work is the development of atomic-level models and *ab initio* quantum chemistry methods that are generally applicable to the chemical decomposition of condensed-phase energetic materials under extreme conditions.

The approaches include quantum mechanics, molecular modeling, Monte Carlo, and molecular dynamics, to yield state-of-the-art methods specifically designed for and tailored to target DoD energetic materials research needs. The following is a list of the principal investigators, universities, and topics that make up the overall MURI project:

- **University of Missouri-Columbia**; Professor John E. Adams; *Gas-liquid heat transfer,*
- **University of Maryland**; Professor Herman L. Ammon; *Crystal models*
- **University of Florida**; Professor R. Bartlett; *Quantum Chemistry*
- **North Carolina State University**; Professor Donald W. Brenner; *Reaction potentials*
- **University of Illinois**; Professors David Ceperley and Richard Martin; *Solid-state quantum mechanics*
- **University of Missouri-Columbia**, Professor Donald L. Thompson (PI); *Reactions dynamics and simulations*
- **University of Minnesota**; Professors Donald G. Truhlar and Christopher J. Cramer; *Solvation models*

The focus of the project is on developing accurate methods for simulating physical and chemical processes in condensed-phase energetic materials. The MURI team is working closely with researchers at DoD labs, which are contributing to the theoretical efforts, providing data for testing of the models, or aiding in the transition of the methods, models, and results to DoD applications. The major goals of the project are:

- Models that describe phase transitions and chemical reactions in condensed materials.
- *Ab initio* predictions of structures and properties of solids at high temperatures and pressures.
- Methods to predict mechanical properties and physical changes in condensed phases, including thermodynamic quantities, phase diagrams, vibrational frequencies, tensile strength, stress/strain relations, and densities.
- Simulation methods to predict chemical decomposition in condensed phases, particularly ignition and sensitivity in response to heating and shocking.
- Methods for predicting temperatures of the condensed phases and flames resulting from physical and chemical changes, including a predictive model for the "heat feedback" from the flame to burning surface.
- Methods for predicting solvation and separation for energetic materials in supercritical fluids.

Technical Progress

The following are descriptions of the components that make up the overall project.

Structure and Density Predictions for Energetic Materials
(Herman L. Ammon, Department of Chemistry and Biochemistry**,** University of Maryland, College Park, MD)

The discovery of new energetic materials can be facilitated with computer modeling and simulation technology for the identification of compounds with significant advantages over materials currently in use. The quantitative estimation of properties such as the heat of formation, density, detonation velocity, detonation pressure and sensitivity can screen potential energetic candidates and permit the selection of only the most promising substances for laboratory synthesis, measurement of properties, scale-up, testing, etc. Thus far, our work primarily has involved developing computer codes and procedures for the prediction of the crystal structures of small, covalent C-H-N-O-F containing molecules. The calculations give solid-state densities and heats of formation and the hypothetical structures can provide valuable information of sensitivity estimates.

Our model-MOLPAK-refinement procedure to predict the most probable crystal structure from a rigid molecular model involves three steps: (1) a model for the compound of interest (the search probe) is obtained from *ab initio* quantum mechanical geometry optimization (usually B3LYP/631G* or 631G**); (2) determination of thousands of possible crystal structures for the search probe (MOLPAK program, MOLecular PAcKing); (3) refinement (WMIN, monopole electrostatics, or DMAREL, distributed multipole electrostatics) of the unit cell parameters, search probe orientation and position by lattice energy minimization for the best of the crystal structures derived in step 2. The most probable structure is identified by a combination of (lowest) crystal lattice energy and (highest) density. In tests of molecules with known crystal structures, the experimental structure is identified by the energy criterion in 80% of the cases and, for the other 20%, the correct structure is among the half-dozen lowest energy predicted structures.

In WMIN, the crystal lattice energy (E) is calculated from the sum of all atom-to-atom interactions between a central molecule and its neighbors.

$$E_{WMIN} = \sum \{332.17[q_i q_j r_{ij}^{-1}] - A_i A_j r_{ij}^{-6} + B_i B_j \exp[-(C_i + C_j)r_{ij}]\}$$

The terms are: q_i = Coulombic charge on atom i; r_{ij} = atom i to j distance; $A_{ij} = (A_i * A_j)^{1/2}$, $B_{ij} = (B_i * B_j)^{1/2}$, A_i and B_i are empirical coefficients for atom i; C_i is similar to a van der Waals radius for atom i. The DMAREL potential is similar with a distributed multipole derived electrostatic term (631G** basis set) in place of the WMIN monopole. The A and B coefficients are optimized by fitting experimental and calculated crystal lattice data with simplex, gradient, and least squares methods. Despite the paucity of experimental enthalpies of sublimation to provide lattice energy standards, the parameterizations provide a good set of coefficients, which translate into more sensitive and definitive lattice energies, structure refinements and accurate predictions. Currently, A and B coefficients have been determined for 69 C, H, N, O, F, S and Br atom types.

The WMIN program, developed at Oak Ridge National Laboratory about 1980, is undergoing a complete re-write. The new code will incorporate modular, modern Fortran and have improved transparency and portability. Major additions will include A and B cross terms for all atom-to-atom interactions to facilitate the handling of special contacts such as H-bonding, analytical derivatives in place of the present numerical quantities, facilitated handling of multiple non-covalently linked groups in the unit cell and intramolecular optimization.

The search probe model obtained from *ab initio* MO geometry optimization describes a molecule free of crystal packing effects. Although a rigid probe is adequate for many packing calculations, there are cases in which the incorporation of conformational flexibility as part of the packing process is required. The flexibility problem has been addressed by the development of the ROTPAK program (ROTational PAcKing) that allows defined conformational changes to accompany the packing processes. The "best" structures represent minima in the total (intra plus intermolecular) energy. Although conceptually simple, the process is complicated by (1) the determination of the intramolecular energy and (2) achieving a proper balance between the intra and intermolecular energies. With the use of the PM3 semi-empirical method to estimate intramolecular energies, ROTPAK has been used to successfully predict the crystal structures of the nitrocubanes, 1,3,5-triazido-2,4,6-trinitrobenzene, N-cyano-N-nitrotolylamine and 2-methyl-4,5-dinitroacetamide starting with B3LYP/631G* optimized models.

Sensitivity, the ease with which a material undergoes a violent reaction or detonation, can be triggered by numerous stimuli such as impact, shock, friction, thermal and electrostatic sources of energy. A number of molecular structure-sensitivity relationships have been found over the years and good correlations observed within families of energetic materials. Sensitivity is perhaps the most complicated and least well understood of the various derivative properties of energetic materials. The following areas will be investigated. (1) We will further explore the utility of the density of states relationship of Kunz, which requires the crystal structure and appropriate *ab initio* crystal lattice calculations. (2) Additionally, possible relationships between impact and friction sensitivity and bond strength plus lattice energy will be investigated. The basic idea is that impact has an important frictional or heat component that initially causes disruption (melting or deformation) of the crystal lattice followed by homolytic cleavage of the weakest bond in the molecule followed by detonation. Lattice energies are available from WMIN/DMAREL calculations and bond energies (e.g. $C-NO_2$, $N-NO_2$, $O-NO_2$) from *ab initio* calculations of the energies of the appropriate framework and nitro group radicals. (3) We have observed previously a correlation between the impact sensitivity and hydrostatic compressibility (from molecular dynamics calculations) for a variety of energetics. For example, the impact sensitive PETN is more compressible than the relatively insensitive TATB. This will be investigated further. (4) The lattice potentials developed can be utilized to explore the relationship between crystal orientation and detonation. In PETN, for example, the orientation to shock initiation and detonation is consistent with steric hindrance to sheer at the molecular/crystal level.

Continuing and future work
1. MOLPAK and ROTPAK preliminary searches. Adjust the intermolecular coefficients to provide better hypothetical structures for subsequent lattice optimization.
2. ROTPAK. Continue development with near-term focus on intramolecular energy evaluation and handling of multiple-bond flexibility.
3. MOLPAK/ROTPAK. Merge rigid and flexible molecule codes to a single unit with complete capabilities of each.
4. Continue force field coefficient optimization for WMIN and DMAREL. Extend to new functional groups and H-bonding.
5. Structure selection. Investigate other criteria (presently use lattice energy and density), such as a comparison of patterns of intermolecular contacts with known crystal structures, to identify the best (correct) hypothetical structure from a prediction set.

6. Complete the recoding of WMIN with a new lattice refinement program with the following properties: (1) Fortran-90 code that will execute on any computer platform; (2) analytical derivatives; (3) coupled inter and intramolecular refinement; (4) separate atom(i)-atom(j) intermolecular potentials; and (5) anisotropic potentials.

7. Prediction package. Couple the various procedures into a seamless package that would include: (1) structure optimization; (2) structure prediction and selection; (3) solid-state heat of formation calculation; and (4) property calculations (e.g. Cheetah).

8. Sensitivity. The structure prediction and lattice potential work will serve as a platform to examine impact/shock and friction sensitivity. Several mechanisms that will be investigated are compressibility, (weakest) bond breaking and lattice energy and steric hindrance to sheer.

Personnel:
Herman Ammon, Professor
Zuyue Du, research associate
Sayta Prasad, sabbatical associate (Physics, Ranchi Univ, India)
Ed Wells, graduate student associate and programmer
Nicole Dueker, undergraduate assistant
Interactions with the energetic material community:
Dr. Betsy Rice (Aberdeen Research Laboratory)
Dr. Ed Byrd (Aberdeen Research Laboratory)
Dr. Alfred Stern (Senior Research Scientist/Technical Consultant for Energetic Materials,
    NAVSEA, Indian Head, MD)
Dr. Willam Koppes (NAVSEA, Indian Head, MD)
Dr. Rao Surapaneni (Chief, Explosives Research and Technology, Picatinny Arsenal)
Dr. Paritosh Dave (Picatinny Arsenal, NJ)
Dr. Robert Chapman (Naval Air Warfare Center, China Lake, CA)
Dr. Philip Eaton (Univ. of Chicago)
Dr. Harold Shechter (The Ohio State Univ.)
Publications:
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• "Crystal Structure Prediction of Small Organic Molecules: a Third Blind Test," G. Day, W .D. S. Motherwell, H. L. Ammon, J. D. Dunitz, A. Dzyabchenko, P. Erk, A. Gavezzotti, D. W. M. Hofmann, F. J. J. Leusen, J. P.M. Lommerse, W. T.M. Mooij, S. L. Price, H. Scheraga, B. Schweizer, M. U. Schmidt, B. P. van Eijck, P. Verwer, *Acta Crystallogr.*, 2004, in preparation.

First Principles Simulations of Energetic Materials
(David Ceperley and Richard Martin, Department of Physics, University of Illinois, Urbana-Champaign)

The overall goal of the group at the University of Illinois Urbana-Champaign is to enable first-principles simulations of energetic materials that are accurate and useful. These methods will become robust tools for prediction of the properties of materials under extreme conditions, especially high temperature and pressure. The work focuses primarily upon quantum Monte Carlo (QMC) methods, the only known approaches that can simulate materials

directly from the fundamental equations for interacting nuclei and electrons. Two QMC methods are under development: Path Integral Monte Carlo and Coupled Electron Ion Monte Carlo. The primary applications are to materials containing first row elements H, C, N, and O, including selected benchmark calculations for definitive comparison with experiments, and simulations of materials under conditions beyond the capabilities of direct experimental analysis.

Code & Algorithm Development:

A particular focus in our work under this grant is to develop new methods and codes. During this year we have made significant progress in writing new quantum Monte Carlo codes that will allow calculations on much more complicated systems and to effectively use more powerful computers. Part of this work involves the PIMC codes we have developed to simulate systems of electrons and protons at high pressures and temperatures. This is a uniquely powerful tool for simulations as demonstrated by our work making detailed comparisons[1] with other types of models and predictions of the results of shock wave experiments on deuterium.

There is a need to develop new approaches that allow the simulations to be feasible at lower temperatures and for materials other than hydrogen. Our recent progress is in the development of the coupled electronic-ionic Monte Carlo (CEIMC) simulations.[3] In this method, one moves the ions classically while calculating the electronic potential (i.e. Born-Oppenheimer) with QMC. In the last 2 years, this method has been tested on molecular and metallic hydrogen composed of up to 100 atoms at temperatures as low as 300K. Our studies of the method applied to hydrogen, show that it has the same order of computational demands, but can be more accurate than Car-Parrinello plane-wave methods. The processing power of current multi-processors is enough that significant applications can already be envisioned. We have developed "reptation" algorithms allowing us to determine energy differences and forces much more accurately than previously and new more efficient methods of moving the electrons. We have also implemented (for the first time) constant pressure QMC methods, much more convenient for simulation of energetic materials. Tests for non-hydrogenic systems are needed to find the performance of the algorithms on a broader spectrum of applications. We have begun constructions of such methods to be able to apply the CIEMC method to energetic materials at finite temperatures, in particular to allow use of more general wavefunctions and pseudopotentials.

The calculation of forces is an outstanding problem in Monte Carlo methods. One of the main reasons keeping QMC methods from becoming a realistic alternative to density functional theory (DFT) based techniques is the lack of an efficient estimator for nuclear forces: e.g. they are needed in molecular dynamics simulations. In the framework of independent-particle DFT theories, nuclear forces are computed with the Hellman-Feynman theorem: the force acting on a given nucleus is equal to the electrostatic force due to the charge distribution surrounding it. This simple result cannot be systematically exploited in QMC due to the divergent variance of the corresponding estimator. Possible solutions to the QMC force problem have been suggested but none of them has gone beyond applications to diatomic systems. We have come up with two new estimators[4] based on the observation that the s-wave component of the density, responsible for the divergent variance, gives no contribution to the force and can be therefore excluded. The key feature of these estimators is their simplicity; this makes them straightforward to apply to many-body systems. For variational Monte Carlo, this leads to a direct way to calculate all components of ionic forces at once. In diffusion Monte Carlo (DMC), since the force is calculated using the electronic density, forward walking or reptation QMC is needed for unbiased results. A nice

feature of one of our solutions is that it retains the local character of the original estimator making its DMC implementation free of uncontrolled approximations. Our results for various molecules (CH_4, NH_3, H_2O, Li_2 H_2) are more accurate than any other method and are the first QMC results for polyatomic molecules. We have also worked on integrating a DFT code with our QMC code in order to make the search for stable structures as automatic as possible. Nuclear configurations are moved according to the stochastic gradient approximation. The results of this work were presented at meetings and a paper has recently been submitted.

Applications

An important part of our work is application to real problems of current interest. The first step in this work is to carry out DFT calculations; which can often provide accurate predictions and can be used to generating trial functions (and trial forces) in QMC calculations. During this period (in work partially supported by another grant) we have brought to fruition our work on nitrogen at high pressure and temperature, as well as predictions of new structures of nitrogen that are metastable at low pressures and temperatures. Nitrogen is a component of many high-energy density materials, and elemental nitrogen itself may be meta-stable in high-energy phases. Nitrogen at high pressure has presented a major challenge for many years, with large disagreement of theory and experiment [5]. However, recent experiments[6] have observed transitions and suggest the exciting possibility that it is sufficiently meta-stable that it could be a candidate energetic material with very high energy per unit mass. Our simulations find competing meta-stable structures separated by large energy barriers, consistent with experiment. The most exciting result is described in a paper that has been submitted [7] – a hexagonal metallic chain structure that is readily derived from the known high-pressure molecular ε phase and energetically equivalent to the lowest energy high-pressure structure found before. Comparison of the energy with other structures is shown in Fig. 1.
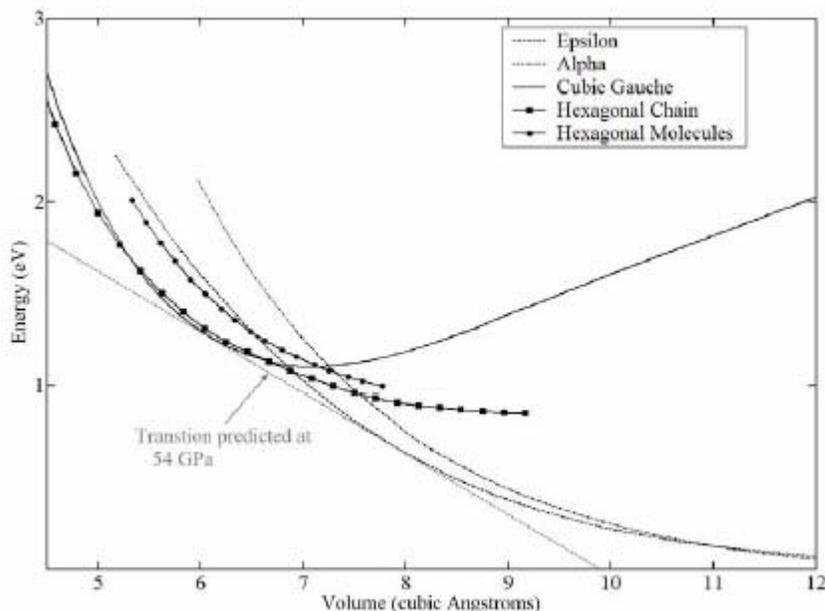

Figure 1. Energy vs. volume for the known molecular phases of nitrogen, the previously predicted cubic gauche phase, and the new phases found in our work. The hexagonal chain is metallic and is essentially the same or more stable than previously studied phases.

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Our work resolves a major puzzle and shows the importance of performing signification *ab initio* simulations that revealed the new structure. These were not observed in work that was limited to structures derived from a simple cubic form. This work was presented at APS March (2004) [8]. These simulations were done with the SIESTA code[9] which is an efficient local orbital code capable of accurate density functional simulations. This is important because this is perhaps the most appropriate code available at present to treat the condensed forms of complex energetic materials.

We have also carried out studies of oxygen in molecular O_2 and ozone O_3 forms, and various non-molecular crystalline forms. The former calculations are meant to better understand the structure of oxygen and ozone in molecular solid forms, and the test the methods using the SIESTA code applied to molecular crystals. The simulations of high-pressure non-molecular phases such as bcc, fcc, and sc have been carried out to provide input that can be used to determine universal force field models. During the summer of 2004 we will results [10] to Prof. Brenner and we anticipate continued interactions with MURI participants Ammon, Brenner, and Thompson. One interesting result is the large effects of magnetic transitions that lead to large changes in energy that modify the order of structures at intermediate pressure ranges. This presents difficulties for the empirical models that are yet to be resolved. They calculations are in fact relevant to oxygen at very high pressure, and they show that simple cubic (sc) is the favored structure for a large range of pressures.

We have started work on molecular crystals of high energy density materials, with the goal to correlate the electronic properties of the molecular crystal - in particular, the band gaps – with to impact sensitivity of nitro aromatic explosive materials.

Future Work

We will complete our on-going investigation of nitrogen at high pressure and temperature. Nitrogen is a component of many high-energy density materials, and elemental nitrogen itself may be meta-stable in high-energy phases. Our simulations find competing meta-stable structures separated by large energy barriers. The most exciting result is a new hexagonal metallic chain structure that is readily derived from the known high-pressure molecular ε phase and energetically equivalent to the lowest energy high-pressure structure found before. This explains many aspects of recent experiments, which indicate metastable structures, and opens the possibility of metallic nitrogen. A paper has been submitted and we will finalize the publication.

We are now carrying out full QMC calculations of predicted structures of nitrogen to verify if they are indeed stable. This work is in progress and detailed comparisons with the DFT predictions will establish the most accurate results possible by any theoretical method available today. Preliminary work reported at the MURI meeting in October, 2003, shows that the structures are in general agreement with the DFT predictions; however, we have not yet reached the final conclusions due to difficulties in converging the energies with the extreme precision needed to quantify small energy differences between very forms of nitrogen with completely different bonding and electronic band structure.

We will continue work on oxygen in molecular O_2 and ozone O_3 forms, and on crystalline forms to provide further input for universal force field models, in conjunction with the work of Professors Ammon, Brenner, and Thompson.[10]

We will also complete work started on high energy density materials, to correlate both structure and electronic properties of the molecular crystal to impact sensitivity and other

properties of nitro aromatic explosive materials. This work is in perogress and a paper is being written.[11]

  We will continue our work to develop coupled electronic-ionic Monte Carlo (CEIMC) simulations [See D. Ceperley, M. Dewing and C. Pierleoni, (physics/0207006), in proceedings of SIMU conference, 2001, Springer-Verlag, eds. Nielaba et al.]. In this method, one moves the ions classically while calculating the electronic potential (i.e. Born-Oppenheimer) with QMC. The outstanding problem in this and other Monte Carlo methods is the calculation of forces. We are developing a new approach for force estimators based on the observation that the s-wave component of the density, responsible for the divergent variance, gives no contribution to the force and can be therefore excluded. The key feature of these estimators is their simplicity; this makes them straightforward to apply to many-body systems. We have also worked on integrating a DFT code with our QMC code in order to make the search for stable structures as automatic as possible. Currently we are writing up results on nitromethane (CH_3ONO) which will continue in this period.[12] We will work toward combined DFT/QMC simulations of such materials.[13]

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13. S. Chiesa, E. Bukhman, D. M. Ceperley and R. M. Martin, in progress.

Interactions with other MURI participants and Army Research Lab personnel
Professors Ammon, Brenner, and Thompson; Drs.William Mattson and Betsy Rice.

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- Chiesa S, Mella M, Morosi G "Estimate of the positron-electron annihilation rate, " AIP Conf. Proc. **690**, 376 (2003)

Papers presented at meetings (exclude those published in conference proceedings)

PLACE		Date	Title
Fort Worth TX	Colloquium	10/25/2002	High Pressure Hydrogen
W Lafayette ID	Seminar	11/8/2002	High Pressure Hydrogen
Princeton NJ	Stochastic Problems	12/9/2002	Coupled Electron Ion Monte Carlo
Trieste,IT	Total Energy	1/16/2003	Coupled Electron Ion Monte Carlo
Minneapolis MN	ES2003	5/20/2003	Localization in a hydrogen chain
Aberdeen MD	MURI Meeting	10/17/2003	Progress Report
Montreal Canada	APS Meeting	3/22/2004	Nuclear Forces in QMC
Montreal Canada	APS Meeting	3/24/2004	New Phases of Nitrogen at high pressure
Rutgers U	ES2004	5/20/2004	Nuclear Forces in QMC
Leiden, Holland	Lorenz Workshop	7/20/2004	Coupled Electron Ion Monte Carlo

Manuscripts submitted, not yet in print.
- S. Chiesa, D. Ceperley and S. Zhang, "A new estimator for nuclear forces in Quantum Monte Carlo," to be submitted Phys. Rev. Letts, 2004.

- W. D. Mattson, D. Sanchez-Portal, S. Chiesa and R. M. Martin, "Prediction of new phases of nitrogen at high pressure from first-principles simulations ", submitted to Phys. Rev. Lett. 2004.
- W. Mattson, D. Sanchez-Portal, S. Chiesa, R. M. Martin, "New crystalline phases of Nitrogen at high pressure ", [J27.004] Am. Phys. Soc. Meeting, March, 2004.
- X. Cheng, S. Chiesa, and D. M. Ceperley, "Quantum Monte Carlo calculations for some nitro and amino molecules".
- X. Cheng, S. Chiesa, and R. M. Martin, "Study of the Band Gaps of Some Nitro Aromatic Explosive Materials and the Possible Relation to Impact Sensitivity".

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Ab-initio **Potential Energy Surfaces and Gradients for Chemical Reactions**
(Rodney J. Bartlett, Tom Hughes, Luis Galiano, and Joshua McClellen
University of Florida, Quantum Theory Project, Gainesville, Florida)

Goals:

To develop and apply quantum chemical methods to provide reliable information about potential energy surfaces for energetic molecules, undergoing decomposition and reaction. This includes detailed studies of unimolecular decomposition and the alternative paths that will likely be encountered with additional interactions in the condensed phase. Systems of interest include nitramine, dimethylnitramine, nitromethane, methylnitrite, RDX, TNAZ, and Fox 7. The hope is to provide accurate results for potential energy surfaces that can be used to define classical potentials, primarily by Don Brenner, and be used in simulations by Don Thompson and Betsy Rice.

To accomplish the above, we use coupled-cluster methods augmented by new developments we have made for larger molecules, like our new singular value decomposition (SVD) approach that leads to 'compressed' coupled-cluster equations; and the use of frozen natural orbitals (NO) to reduce the effective basis set for large scale CC calculations. The NO-CC approach requires the development of analytically computed forces (gradients) to enable the effective search of potential energy surfaces for structure and transition states. We are also exploring new density functional methods to assess their ability to describe energetic systems, at a lower cost.

We are also developing a 'transfer Hamiltonian' that is meant to be a low-rank operator that enables the accuracy of CC theory to be maintained, but for much more complicated

systems. In this way, we hope to be able to do simulations with quantum mechanical forces that can be generated 'on-the-fly.'

Progress

We have done a number of calculations on nitramine and dimethylnitramine and related systems to assess the errors in the calculations and explore basis set extrapolation procedures, particularly for forces. Many energy extrapolation methods have been used, but for entirely satisfactory results it is equally important to know the forces at the basis set limit to converge transition state structures and associated activation barriers.

We introduced our singular value decomposition (SVD), 'compressed" coupled-cluster method in two papers (1,2) where the detailed results can be found. The basis idea is that there is substantial basis set linear dependency in high-level, correlated quantum chemical calculations. SVD is a way to remove much of this dependency by identifying an alternative set of terms that are weighted by their numerical importance. In normal CC theory, the number of T_2 amplitudes is o^2v^2 for i,j,,,occupied and a,b,... unoccupied orbitals. For triple excitations we require o^3v^3, etc. SVD leads to an alternative expansion in terms of amplitudes $t_2(X,Y)$ instead of $t_2(ia, jb)$, where the X index is a weighted (a_i) and Y a weighted (b_j), so that there a many fewer indices than in normal coupled-cluster theory. This is particularly important as we go to higher amplitudes like T_3, where a computational $\sim n^8$ procedure can be dramatically reduced.

Similarly, the use of frozen natural orbitals can have a similar effect, but to use them effectively, requires the development of new analytical gradient methods for such calculations to permit structures and transition states to be obtained. We have recently worked on this problem(3).

The concept of a 'transfer Hamiltonian' has been developed, formally from wavefunction theory, by showing that an exact one-particle operator exists that can provide the exact ionization potentials, exact energy, and exact density matrix for a molecule (4). In the case of exact dft, by using the density as the critical quantity, we know that the one-particle operator, the Sham Hamiltonian, will provide the molecule's exact density, its ionization potential as the negative eigenvalue of the highest occupied molecular orbital, and energy from inserting the density into the energy functional. Consequently, if we can arrange to build such a simplified one-particle, typically, parameterized Hamiltonian, by, eg, insisting that it reproduce the correct structures, densities, and bond-breaking results in coupled-cluster calculations, and demonstrate that its form saturates for small clusters, we then have a tool that permits the very rapid generation of quantum mechanical forces to drive molecular dynamics. In particular, we are doing this for nitromethane, where we perform CC calculations on the dissociation paths, and then go to two three,... nitromethanes until all the parameters in the chosen form of the Hamiltonian are fixed regardless of the number of nitromethane molecules; then we should expect that the Hamiltonan so defined, would be able to describe many nitromethane molecules with CC accuracy. Only such a tool can be expected to provide reliable, quantum mechanical results in a time-frame suited to MD. The seamless transition between the transfer Hamiltonian and the classical potentials is particularly important for realistic sized condensed phase systems.

Publications:

● T. Kinoshita, O. Hino and R.J. Bartlett, "Singular value decomposition approach for approximate coupled cluster method," J. Chem. Phys. **119,** 7756-7762 (2003).

- O. Hino, T. Kinoshita and R.J. Bartlett, "Singular value decomposition applied to the compression of T_3 amplitude for the coupled cluster equations," J. Chem. Phys. **121**, 1206-1213 (2004).
- A. Taube, A. Perera and R. J. Bartlett, to be published.
- A. Beste and R. J. Bartlett, "Correlateed Independent Particle Method: Numerical Results," J. Chem. Phys., submitted

Presentations:
- Sept 2004 – Electronic Structure: Principles and Applications (ESPA-2004), Valladolid, Spain
- May 2004 – Response Theory and Molecular Properties, Sandbjerg Manor, Sonderborg, Denmark
- Feb 2004 – "Correlated Orbital Theories: On wavefunction theory and density function theory, the development of an exact one-particle theory for molecules,",Theory and Applications of Computational Chemistry, Gyeongji, Korea
December 2003 – "Atomic Scale Materials Design: Modeling & Simulation" Materials Research society, Boston, MA
- October 2003 – "*Ab initio* Predictions of PES for Chemical Reactions," Review of Energetic Materials DURINT and MURI Programs, Aberdeen, MD
- September 2003 – "Metastable Molecules in Ground and Excited States," 2nd Advanced Energetics Technical Exchange, Aberdeen, MD
- September 2003 – "Coupled-cluster Methods and Their Applications to Energetic Molecules," 226th ACS National Meeting, New York, NY
- August 2003 – "High level Couple Cluster Theory: What Did We Learn?" 8th European Conference on Quantum Systems in Chemistry and Physics, Spetses, Greece
- July 2003 – "*Ab Initio* Density Functional Theory," Electron Correlation: *Ab initio* Methods and Density Functional Theory, Satellite Meeting of the XIth International Congress of Quantum Chemistry, Bad Herrenalb, Germany
- April 2003 – "Frontiers in Theoretical Chemistry," a Symposium in Honor of Prof. Rudolph A. Marcus, Los Angeles, CA
March 2003 – "From Wave Function Theory to Density-Functional Theory and Back," 225th ACS National Meeting, New Orleans, LA
- October 2002 – "Scalable Software for Computational Chemistry," Grid Computer Conference, University of Kentucky, Lexington, KY
- October 2002 – "*Ab initio* Predictions of PES for Chemical Reactions," MURI Kick-off Meeting, Aberdeen, MD
- September 2002 – "Large Scale Dynamics with Quantum Mechanical Forces," Symposium and Summer School on Nano and Giga Challenges in Microelectronics Research and Opportunities, Moscow, Russia
- September 2002 – "Predictive Theory from Molecules to Materials," Science at the Edge, Michigan State University
- July 2002 – "Advances in Electronic Structure Theory: Current Trends and Future Prospects," International Conference of Theoretical Chemical Physics, IV, Marly-le-Roi, France
- June 2002 – "Predictive Theory from Molecules to Materials," Symposium to Initiate Joint Ph.D. Program between France and the United States, Strasbourg, France
- June 2002 – "Large Scale Simulations with Quantum-Mechanical Forces," European Materials Research Society Spring Meeting, Strasbourg, France

Students Supported by MURI:
- My most recent Ph.D. DeCarlos Taylor, is now on an NRC postdoctoral position at the Army Research Laboratory.
- Several other students have been partly supported by this MURI. Dr. Ariana Beste, Ph.D., 2004, now at Oak Ridge national Laboratory; Dr. Tom Henderson, Ph.D., 2004, now at the NMRC, Cork, Ireland; Dr. Anthony, Yau, Ph.D., 2004, now at ACES QC, Gainesville, FL, and current students: Josh McClellan, Tom Hughes, and Luis Galiano.

Interacgtions with Army Scientists:
Dr. DeCarlos Taylor
Dr. Steve Bunte
Dr. Betsy Rice
Dr. Shashi Karna
Dr. Cary Chabalowski

Quantum-Based, Reactive Potentials for Simulating Shock Dynamics of Condensed-Phase Energetic Materials
(Donald W. Brenner, Materials Science and Engineering Dept., North Carolina State University, Raleigh, N.C.)

We are currently developing a transferable and robust analytic reactive potential for C, H, O and N containing species that is valid in both the molecular and condensed phase regimes and that allows chemical reactivity through all changes of detonation and shock propagation, as well as slower deflagration processes. The analytic functional form is based on a chemically sound bond-order formalism that has proven extremely powerful for describing reactivity in hydrocarbon systems. Accurate first principles quantum-mechanical calculations are being used to both determine appropriate functional forms and parameters entering this formalism, and to validate specific chemical reaction paths and rates for unimolecular dissociation and recombination produced by the analytic potential. These computationally efficient potentials are enabling large-scale, three-dimensional molecular dynamics simulations to be carried out at the Army Research Laboratory that will predict system properties related to shock initiation and detonation of a wide range of both existing and potentially safer and more powerful high explosives (i.e. molecular design).

Progress:

A reactive empirical bond order potential for N_xH_y species has been completed, and the functions and parameters sent to Dr. Betsy Rice at the ARL for incorporation into the current DoD molecular shock modeling codes. Dr. Rice has completed the initial coding needed to derive forces from the potential energy expression, and will initiate molecular modeling simulations with this code and forces. This potential will initially be used in conjunction with Dr. Rice and Prof. Thompson to model shock chemistry of liquid hydrazine.

This version of the N_xH_y potential is consistent in form with our C_xH_y potential previously developed, and consistent with a new potential for CHO species developed by Prof. Sinnott at the University of Florida. We have begun building on this common functional form by combining it with new bonding and charge screening screening approaches developed as part of

our MURI effort (see prior report). Currently, effective pair terms in this many-body potential have been developed for all pairs of atom types except for N-O.

The fitting data base for our N_xH_y potential is extensive, and includes bond energies and bond lengths for the molecular species H_2, N_2, NH, NH_2, NH_3, HNNH, H_2NNH_2, H_3NNH_3, $HNNH_3$, the energy barrier for the inversion of NH_3, and condensed phase properties of liquid ammonia. This is the first potential energy expression to address the properties of each of the species in a single functional form, a feature that will be key in utilizing the potential to characterize the properties of hydrazine. Because many of the properties of hydrazine are reasonably well known from experiment, the results of simulations using our potential will both help validate the potential, as well as lend important new insights into the reactive dynamics of these systems.

The Sinnott oxygen potential was not fit to nor validated against high-pressure phases of oxygen that may play a role as transient intermediates in detonating solids. To validate the potential for this regime, Prof. Martin's group has used first principles methods to calculate the energy of oxygen in face centered cubic, simple cubic and diamond cubic lattices as a function of lattice constants. Both spin restricted and spin unrestricted calculations were carried out. Comparisons between these calculations and the energy-lattice constant relations of the Sinott potential are currently being quantified.

An informal workshop was held at North Carolina State University on June 29 and 30, 2004. Hosted by Prof. Brenner and the NC State Department of Materials Science and Engineering, a purpose of this workshop was to discuss common issues and progress related to the development of many-body interatomic potential energy functions by some of the leading university researchers in the southeast. The workshop was attended by Prof. Sinnott and Prof. Simon Philpot of the University of Florida, Prof. Steve Stuart of Clemson University, and Prof. Judith Harrison of the Naval Academy, as well as postdocs and students from these groups. Progress on the hydrazine potential being developed in the MURI was discussed by Prof. Brenner, including the new line-of-state screening and topology functions being used to describe bonding range and bonding type between pairs of atoms. Prof. Sinnott discussed her new CHO potential mentioned above. Prof. Stuart described his recent work on variable charge methods in which an effective charge is assigned to an atom according to its environment using constraints related to the relative electronegativity and hardness of an atom, and how these methods can be incorporated into bond order potentials. Prof. Simon Phillpot discussed his numerical method for calculating long-range Coulomb interactions in which a convenient cut-off radius is chosen and any residual charge is placed at a sphere with the cut-off radius. The method is accurate and convenient to code as an independent subroutine. We are currently exploring the utility methods, including their incorporation into the ARL modeling codes.

Supported Personnel:
Ben Gilbert, graduate student
Kai Wang, research assistant professor

Beyond Steady-State Deflagration Models: Molecular Dynamics at a Gas-Liquid Interface (John E. Adams, T. Szabo, and A. Siavosh-Haghighi; University of Missouri, Columbia, MO 65211)

State-of-the-art models of the steady-state deflagration of an energetic material[1] have proved reasonably successful in reproducing experimental combustion rates in a number of systems. Inasmuch as these models are based on continuum descriptions of the condensed

phases, they are likely to have reached the limit to which they can be extended and enhanced, however, in the absence of detailed molecular information. Furthermore, they necessarily are applicable only to systems in which a steady state has been established and thus are of little direct help in modeling the initiation of combustion. Understanding how a combusting system reaches steady state will require additional insight into the mass and energy balance during the early stages of combustion, with part of that picture being the transfer of energy from nascent gaseous combustion products to the thin liquid film that forms at the surface of a burning solid. Even within the context of the extant steady-state models, though, there is a need for molecular-level data for the implementation and detailed validation of these models, data such as temperature-dependent vapor pressures and a characterization of the gaseous product dynamics in the presence of temperature gradients.

Our initial focus has been on obtaining a basic understanding of the energy transfer from translationally hot gas atoms to a prototypical liquid surface. The simplest non-trivial system that nonetheless has the potential of capturing the gross dynamics of a more complex system consists of atoms interacting through Lennard-Jones forces, a system such as the one investigated previously by Tribe *et al.*[2] Simulations of this system have been performed using the modular DL_POLY_2 code[3], with additional modules being developed as necessary to handle system initialization and the final energy analysis.

We begin by equilibrating a liquid sample at a selected temperature (*NVT* ensemble, periodic boundary conditions, cubic simulation cell) then create an interface (actually, two interfaces) by expanding the simulation cell length in the *z* dimension. (Periodic boundary conditions in three dimensions are maintained following the expansion.) At this point, we can either (1) proceed at constant energy—the system then cools as kinetic energy is converted to potential energy—until a final average temperature is established or (2) continue the simulation at the desired final temperature. (Prior to this final equilibration, the net center-of-mass velocity of the liquid sample, which is an artifact of the way in which the interfaces are created, must be substracted.) These procedures lead to a density contour in the system such as that shown here.
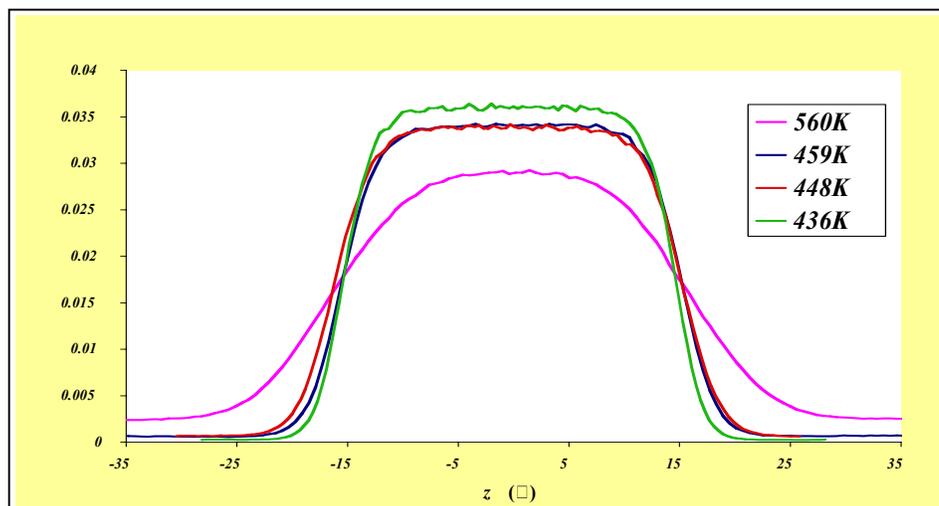
Note that as the temperature of the sample increases, the width of the interfaces also increases. Furthermore, at the highest temperature shown, one easily sees a finite, uniform vapor density in the volume of the simulation cell that initially was empty. The initial configurations for the energy transfer studies are then generated by recording snapshots of this system periodically as the *NVT* simulation proceeds.

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For the actual studies of energy transfer, we direct atoms with a well-defined kinetic energy at the surface configurations generated as described above, the initial positions of these atoms being chosen at random within a plane parallel to the liquid surface and at a distance sufficiently far from it that there is no initial interaction. The energies (and scattering angles) of these atoms are then analyzed at the point that (1) they rebound from the surface and reach the plane from which they initially were injected into the system ("scattered atoms") or (2) the trajectory times exceed a maximum value, beyond which the atoms are assumed to be trapped and equilibrated with the surface ("trapped atoms"). However, if at the maximum trajectory time an atom is moving away from the surface and experiencing no interactions with other species in the system, then the atom is also counted being "scattered".

The final energy distribution of initially hot atoms directed towards a liquid surface (at a Lennard-Jones reduced temperature of 0.719; the incident angle is 55° with respect to the surface normal) is given in the figure below. Note that the full distribution (labeled "All") is strongly peaked at low energies, a result that reflects the thermal equilibration of trapped species with the surface. (The average kinetic energy of atoms equilibrated with the surface for this system would be 5.44 kJ/mol.)
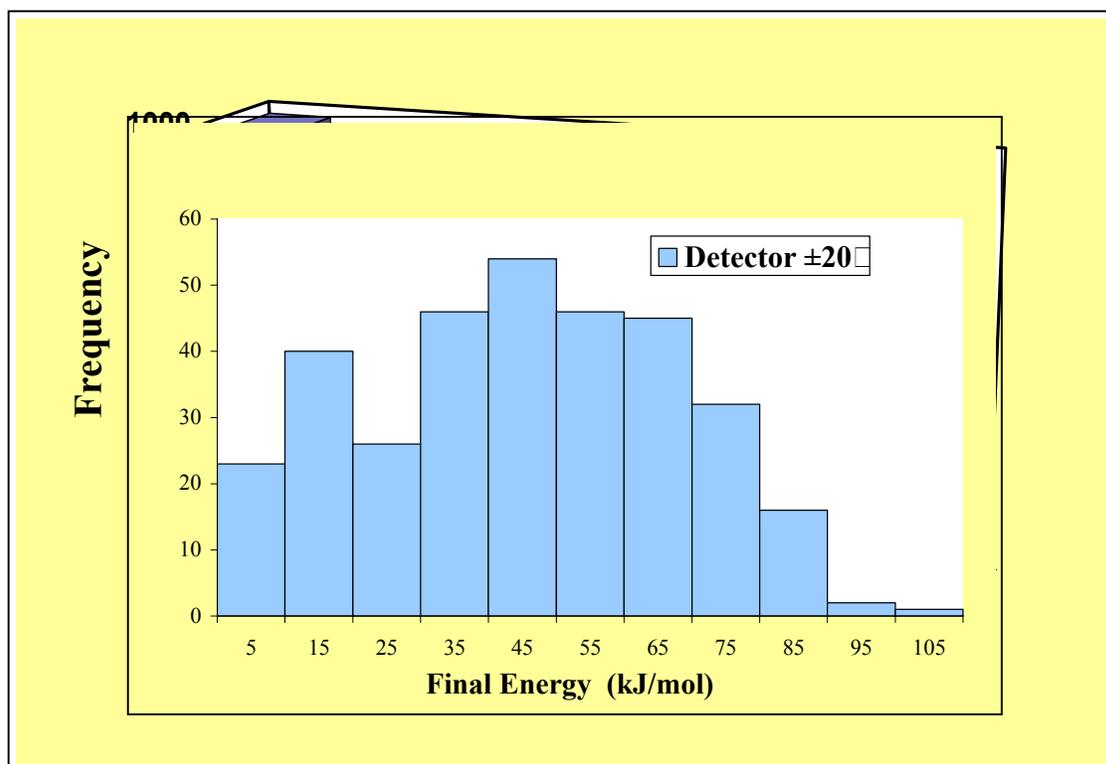
It is interesting to compare these results with those reported by Nathanson and co-workers[2], who investigated atom scattering from a liquid metal surface. (The parameters in the present study have been chosen to mimic those experiments.) In practice, of course, energy analysis in the experiments necessitates the use of a detector having a finite entrance aperture. Thus, if one models the experiment by analyzing the final energies of atoms scattered at the specular angle (and using a relatively large entrance aperture to improve the counting statistics[2]), one finds a very different energy distribution, one that is peaked at about 50% energy transfer, with an average energy transfer that is somewhat less than that.

The key to understanding the relationship between collisional energy transfer and the establishment of a steady-state temperature in a deflagrating energetic material is the dependence of the energy transfer on the surface temperature. The figure below shows a comparison of the scattered energy distributions calculated at two different temperatures (reduced temperatures of 0.719 and 0.923). The distributions in fact are found to be quite similar, but it is important to
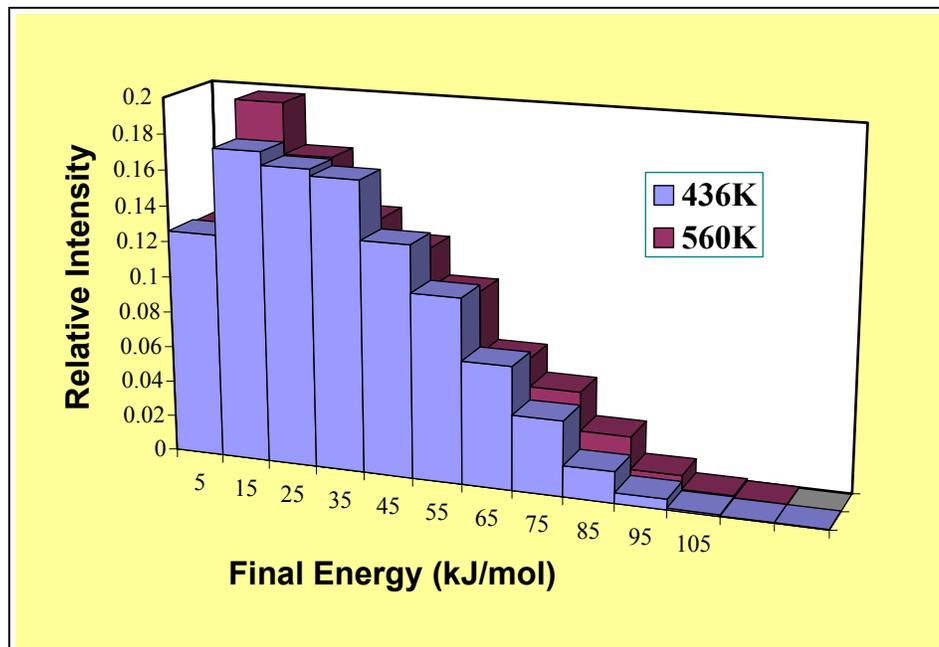

note that these distributions have been scaled in each case by the number of scattered atoms. The significant difference between the two sets of results is that at the lower temperature 80% of the atoms are scattered rather than trapped, while at the higher temperature this percentage drops to 64%. This increased incidence of trapping (and thus thermal equilibration) as the surface temperature increases can be correlated with greater surface roughness—the broader surface contour at the higher temperature also testifies to the temperature-dependence of the surface topology. (Surface roughening was also posited by King et al., to explain the experimental scattering of argon from perfluorinated polyethers.[4]) A complete analysis of the surface temperature dependence of energy transfer in our prototype system is in its final stages, with a manuscript describing the work being prepared for submission by the end of the year.

We also are pursuing an investigation of a practical energetic material, nitromethane, for which potential parameters and a characterization of the melting behavior are available in the work of Agrawal, Rice, and Thompson.[5] These calculations are significantly more demanding than are those relevant to the Lennard-Jones system in that we include all internal degrees of freedom of the nitromethane molecules. (In an extension of the present work, we will freeze the internal coordinates of the molecules and assess the extent to which the collisional energy transfer is altered when molecular vibrations no longer provide an accessible energy sink.) The surface contour in this system is given in the figure below.

Nitromethane, 360K

z (angstroms)
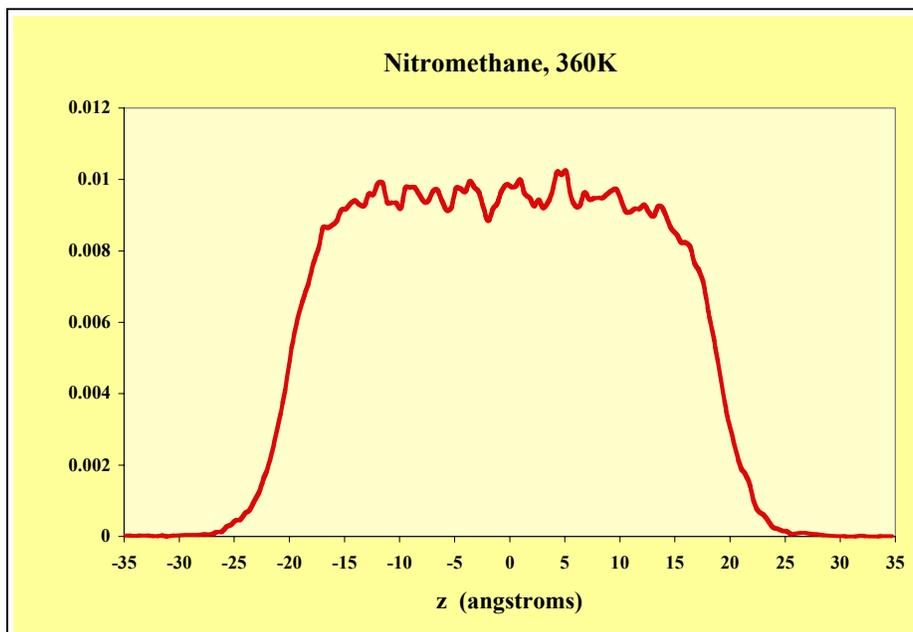
While this work is still ongoing, an example of the system configuration is shown here. The important point to recognize in examining this configuration is that the surface layer is by no means simple, that it is rough on a microscopic scale. Accordingly, an atom colliding with this surface is expected to experience a high probability of trapping. (In an example trajectory computed for this system, 64% of the incident energy was transferred as a result of the collision.) We expect to have a manuscript describing our initial work on this system, work that will include a determination of the equilibrium vapor pressure of nitromethane above the liquid surface, ready for submission by year end.
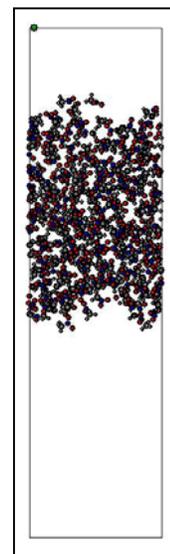
Finally, we have begun looking at ozone as a system that will be useful in connecting the simulations with extant continuum models of deflagration. One would like to use a potential model in this system that correctly accounts for all species present in the system during burning. Work leading to a potential model with the desired properties is presently under development by the Brenner group. We expect to have access to these results shortly.

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4. King, M.E.; Fiehrer, K.M.; Nathanson, G.M.; Minton, T.K. *J. Phys. Chem. A* **1997**, *101*, 6556.
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Development of Methods for Predicting Solvation and Separation for Energetic Materials in Supercritical Fluids

(Christopher J. Cramer, Jason Thompson, Casey P. Kelly, Benjamin J. Lynch and Donald G. Truhlar; Department of Chemistry and supercomputing Institute, University of Minnesota Minneapolis, Minnesota)

The current goal of the MURI work here at the University of Minnesota is to achieve a better understanding of the solubility and other properties of substances in supercritical fluids and to employ that understanding in the development of supercritical fluid technologies for recycling and reclamation of energetic materials. In particular, we plan to model solubility in supercritical fluids because this property has important applications to high-energy materials. We are developing the tools and software for accurate predictive methods and models for solvation of energetic materials in supercritical carbon dioxide; we are implementing them into easy-to-use codes that are freely available via the World Wide Web. Thus Army and MURI researchers will be able to use these models and methods to facilitate the design of practical procedures for extraction, recycling, and reusing materials.

Since the MURI project began in 2002, we have focused on extending existing continuum solvation models to supercritical solvents. Our existing continuum solvation models (i.e., solvation models for ordinary liquid solvents) utilize the generalized Born (GB) model in a self-consistent reaction field step to account for long-range electrostatic effects. Note that the GB model represents the solute as a collection of atom-centered spheres and atom-centered point charges. Our model also accounts for solvation phenomena beyond electrostatics, including cavitation, dispersion, hydrogen bonding, and structural changes taking place in the first solvation shell(s), as well as local changes in the permittivity of the solvent, by modeling these effects as being proportional to the solvent-accessible surface areas (SASAs) of the atoms in the solute. The constants of proportionality are called atomic surface tension coefficients. They contain parameters (called atomic surface tension parameters) that are optimized against a training set of experimentally known free energies of solvation in water and organic solvents and that depend on a set of experimental solvent descriptors of the solvent. Our initial approach for developing a continuum solvation model for supercritical CO_2 is to treat the critical-fluid solvent as a continuum liquid, i.e., a continuous and homogenous medium characterized by the bulk dielectric constant, augmented with surface tension coefficients optimized for liquid solvents, and then optimize a set of solvent descriptors for supercritical CO_2 that are functions of temperature and pressure.

In the rest of this document, a summary of the progress made for this MURI project and a list of publications and manuscripts in preparation of MURI-supported work are given.

Progress:
Improved Charge Models

During the first year and a half of the MURI project, we focused on developing new charge models that provide accurate and reliable charges to use in the GB model. Because diffuse functions may be important for an even- handed description of conformational energies

and of negative functional groups found in many of the compounds of interest, we have developed a new population analysis method, called redistributed Löwdin population analysis (RLPA). This method provides partial atomic charges that are less sensitive to the inclusion of diffuse functions to the basis set than Löwdin population analysis partial atomic charges. We have also created a new class IV charge model, called charge model 3 (CM3). The CM3 charge model uses a semiempirical charge-mapping scheme that is a function of the Mayer bond orders in the molecule. This scheme systematically corrects errors in bond dipoles calculated from low-level charges, such as Löwdin population analysis charges. The CM3 charge model has several improvements over previous class IV charge models developed in our research group. In particular, the CM3 parameters were optimized against a larger and more diverse training set than previous charge models. Second, when diffuse basis functions are used, CM3 maps RLPA charges rather than Löwdin population analysis charges. In addition, the CM3 parameters were chosen so that the resulting charges are not as sensitive to variations observed in the Mayer bond order when diffuse basis functions are included in the basis set. Finally, for some wave functions, CM3 uses a new charge-mapping scheme for solutes containing both N and O.

Validation of Charge Model 3

Our progress in 2003 and at the beginning of 2004 included the validation of the CM3 charge model for predicting accurate charge distributions of high-energy materials (HEMs) and compounds analogous to them. Charge model 3 is a parameterized model, where the parameters have been optimized against a training set of dipole moment data. The training set is large (398 data) and diverse, containing many different types of functional groups that one encounters in organic chemistry. However, the functional groups found in HEMs are either under-represented with respect to other functional groups present in the training set (nitro compounds) or not represented at all (nitramines, for example) in the CM3 training set. To determine whether or not the CM3 parameters are applicable for predicting accurate charge distributions of HEMs, we assembled a test set of compounds, including nitramide, dimethylnitramine (DMNA), 1,3,3-trinitroazetidine (TNAZ), 1,3,5-trinitro-*s*-triazine (RDX), and hexanitrohexaaza-isowurtzitane (HNIW), and compared the dipole moments for different conformations of these compounds (14 in all) calculated using CM3 charges to high-level theoretical density dipole moments. Note that a density dipole moment is calculated from the one-electron density as an expectation value of the dipole moment operator, and density dipole calculations do not provide the partial atomic charges needed for condensed-phase modeling. These tests have shown that partial atomic charges from CM3 can be used to predict dipole moments for these types of compounds with similar or better accuracy as for compounds in the CM3 training set. Furthermore, this good agreement is obtained even when relatively inexpensive wave functions are used for the solute, which is important for larger solutes like HNIW. For the above test set of nitramines, we have also shown that atomic charges calculated with CM3 yields polarization free energies (computed from the GB model) for the condensed phase that are less sensitive to the level of treatment of electron correlation than those given by other methods. This invariance to the level of treatment of electron correlation demonstrated by the CM3 model will be important in future work, which will focus on the further development and testing of different theoretical methods for modeling the solid-state condensation of HEMs.

A New Continuum Solvation Model Based on Charge Model 3

We have also determined a new set of atomic surface tension parameters to be used in conjunction with GB model employing CM3 charges. These new parameters will be used in the optimization of solvent descriptors for supercritical CO_2. They were optimized against 2237

experimental free energies of solvation of solutes in water and 90 organic solvents and 79 free energies of transfer between water and 12 different organic solvents (the free energy of transfer of a solute defines the partition coefficient of a solute between two different solvents). The resulting model, called SM5.43R, can predict free energies of solvation of solutes in water solvent and in organic solvents, provided the solvent descriptors for the organic solvent of interest are known. In addition, SM54.3R predicts aqueous free energies of solvation a factor of one (ions) to two (neutrals) more accurately than the continuum solvation models available in the *Gaussian* electronic structure program and free energies of organic solvation a factor of six to seven (!) more accurately than these models. This represents a resounding success for the new model.

In 2003, we initially optimized SM5.43R parameters for the mPW1PW91 (also denoted MPW25) hybrid density functional method with the 6-31G(d) and 6-31+G(d) basis sets. The mPW1PW91 combines Barone and Adamo's modified version of Perdew and Wang's exchange functional, Perdew and Wang's correlation functional, and a percentage X of exact Hartree-Fock exchange. In 2004, we carried out further SM5.43R parameter optimizations for the MPWX/MIDI!, MPWX/MIDI!6D, and MPWX/6-31+G(d,p) combinations of electronic structure method and basis set with X = 0, 25, 42.8, and 60.6, and for MPWX/6-31G(d) and MPWX/6-31+G(d) with X = 0, 42.8, and 60.6. For each of the five basis sets, we found no significant loss in the accuracy of the model when parameters averaged over the four values of X are used instead of the parameters optimized for a specific value of X. This is a significant result because for a given property of a molecule or reaction, it may be useful to optimize the value of the fraction of Hartree-Fock exchange in MPWX. With an optimized value of X in hand for a particular problem, it is useful to have a solvation model already parameterized for that value of X.

Implementations of RLPA, CM3, and SM5.43R

We have implemented this new model in three quantum chemistry computer programs, namely, GAMESSPLUS, HONDOPLUS, and SMXGAUSS, all of which are freely available on the internet (see http://comp.chem.umn.edu/truhlar). We have made various optimizations to HONDOPLUS (and consequently to SMXGAUSS, which is based on the electronic structure code implemented in HONDOPLUS) to allow it to run four times faster for density-functional theory calculations. In addition to these optimizations, we have also increased the portability of our solvation codes, allowing us to make better use of the computational resources available. These increases to speed and portability have decreased turnaround time to perform calculations for the development of new solvation models.

Development of a Training Set of Solvation Data of Solutes in Supercritical CO$_2$

In addition to the GB model, our continuum solvation model incorporates short-range solvation effects with semiempirical atomic surface tension terms. These semiempirical atomic surface tension terms contain parameters that are optimized against a training set of known experimental free energies of solvation. In order to develop a continuum solvation model for supercritical carbon dioxide, a training set of experimentally determined free energies solvation of various solutes in supercritical carbon dioxide is required. Therefore we carried out a thorough search of the literature on relevant data for supercritical carbon dioxide. As a result of this search, of our reading in this area, and our discussions at the meeting in Aberdeen (October 2002), we came to the conclusion that our modeling input (for deriving new surface tension parameters) for the supercritical aspects of our solvation model will have to be based on solubilities and vapor pressures of pure substances rather than free energies of solvation and

partition coefficients. In contrast, all of our past work was based on starting with free energies of solvation and partition coefficients. So we investigated the effect of this on our studies and our modeling plan.

First we derived the equations relating solubilities, vapor pressures of pure substances, and free energies of solvation to one another in the case of ideal solutions (i.e., when all activity coefficients and fugacity coefficients are unity). Then we created a test set of 85 solutes (both liquids and solids, mainly compounds composed of H, C, N, and O, but also a few halogenated compounds to add diversity) for testing how well the ideal solution equations hold for saturated solutions. This is a very fundamental question in chemical thermodynamics, and this investigation was essential to the design of subsequent steps in our modeling effort. In addition, we were unaware of any tests comparable to our own that have been published in the literature.

For liquid solutes, we found that we can predict solubilities by our methods with comparable accuracy to what we have previously come to expect for free energies of solvation and partition coefficients. We also found that we can use experimental vapor pressures as part of our model when available, but we can equally well predict the vapor pressures that are needed as part of the solubility calculation, and it did not degrade the accuracy of our predicted solubilities. In addition, our predictions were almost as accurate as can be done when experimental free energies of solvation are available.

The results for solid solutes were not as accurate as our results for liquid solutes, but they were still encouraging. Nevertheless, by including both liquid and solid solutes in our tests, we achieved a better fundamental understanding of the issues involved in modeling solubilities, and we opened ourselves to the possibility of incorporating a broader database for developing parameters, a possibility that we will take advantage of and that will be a critical aspect of our model development.

We have started to assemble a training set of solutes with known experimental solubilities in supercritical CO_2 over a wide temperature and pressure range. In order to create a set of generally useful solvent descriptors, this training set includes both high-energy compounds and compounds containing a variety of other functional groups. In addition to searching the chemical literature and submitting data requests to the Army, we have been in contact with Victor Stepanov at Picatinny Arsenal in New Jersey and Lev Krasnoperov (through Dr. Stepanov) at the New Jersey Institute of Technology about measuring solubilities of nitramine compounds using in situ UV spectroscopy. In addition we successfully obtained institutional authorizations to obtain Militarily Critical Technical Data (CPIA M3 and M4 Manual Units), and we purchased a safe to hold this.

Current Research

In order to predict solubilities of high-energy materials in supercritical CO_2, we will need to be able to predict the pure-solute vapor pressure of these compounds. The required solvent descriptors for these types of compounds are not experimentally known, and so we need a method to estimate them. Platts and coworkers have developed a model that can be used to estimate two (Abraham's acidity and basicity parameter) of the four solvent descriptors required for our solvation model.[1,2] This model may be denoted as a fragment model, as it estimates the value of a given solvent descriptor as a sum of contributions from various types of fragments in the solute. These fragments are, in some cases, ambiguous, particularly for N-containing solutes. Because the fragment model proposed by Platts and coworkers can be ambiguous and because it is not available for two (the index of refraction and the macrocopic surface tension) of the four

required descriptors in our solvation model, we are in the process of developing several models comparable to this model. In particular one model correlates solvent descriptor values to the different types of covalent bonds in the solvent, and another model correlates these values to the exposed surface areas of the atoms in the solvent. The former model is also a fragment model, but the fragments are unambiguous. In the exposed surface area model, the only required input is the three dimensional geometry of the solute. Preliminary results show that these models perform as well as or better than the fragment model of Platts and coworkers.

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Manuscripts in Preparation from MURI-Supported Work
• "Fast and Accurate Methods for Predicting Solvent Descriptors," Thompson, J. D.; Cramer, C. J.; Truhlar, D. G.

Method Development and Simulations of Physical Processes and Chemical Reactions in the Various Phases

(Donald L. Thompson, Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma)

The focus of the research at Oklahoma State University is the development of practical methods for simulations and rate calculations of physical and chemical processes in the gas, liquid, and solid phases of energetic materials. The work for this report period focused on the following projects:

• Development of accurate methods for simulating melting and predicting melting points of organic solids.

• Development practical methods for computing reaction rates of reactions in condensed phases.

• Development of methods for fitting *ab initio* potential energy surfaces and for performing direct dynamics simulations.

• Using quantum chemistry methods to determine the reaction pathways for unimolecular and bimolecular reactions of energetic molecules.

Predictive models for condensed phase processes

A significant result of our work during this report period is the development and demonstration of methods for simulating solid-to-liquid phase transitions in energetic materials to predict their melting points. Prior to this grant, working with Drs. Betsy Rice and Dan Sorescu, we developed crystal models for organic materials that accurately describe a wide range of energetic materials. In the current grant we have used these models in studies of melting transitions of energetic materials. The simulation of melting and the prediction of melting points have been considered difficult problems. The difficulty stems from the free energy barrier for the formation of a liquid-solid interface; which can cause superheating in a perfect crystal and thus an overestimation of the melting point of the real material. We have investigated various ways of performing the simulations to determine the most practical one for use in studies of energetic materials. Prior to our work, the simulations had been restricted to atomic solids such as rare gases and metals.[1] We first carried out a series of calculations for argon[2] to test methods which we then extended to nitromethane,[3] RDX,[4] and PETN.[5]

The introduction of vacancies in a crystal eliminates the free energy barrier that causes superheating in a perfect crystal. Alternatively, the simulations can be initiated with the solid in contact with liquid. Molecular dynamics studies of melting of nitromethane using the intermolecular interaction potential of Sorescu *et al.*[6] have been carried out by two methods: (1) void-nucleated melting with the gradual heating of the lattice and (2) equilibration of coexisting liquid and solid phases. The results are in near agreement with each other; the small difference is attributed to the hysteresis effect associated with the direct heating process. The computed values of the melting temperature are in good agreement with the experimental data at various values of pressure ranging from 1 atm to 30 kbar. Since the void-induced melting approach is much easier to use, we have adopted it as the practical approach for predicting melting points of energetic materials. Following this work, which used our well-tested force field for nitromethane, we have extended the studies to RDX and PETN, which we believe will provide critical tests of the models and the melting approaches. We find that the results are sensitive to details of the potential and that for large, complex molecules the simulations are somewhat more

demanding; however, the results, which are currently being prepared for publication, show that approaches that we are using will be effective and practical for predicting melting points.

This work is being done in collaboration with Dr. Betsy Rice at ARL. She will incorporate these methods into the general simulation codes she is developing for Army applications.

Practical Rate Calculation Methods

While the main thrust of the work has been explicit MD simulations of processes in condensed phase energetic materials, we are also interested in developing accurate methods for rate calculations that complement the results of simulations, especially methods that can be used to either save computer time or to treat reactions that cannot be dealt with in a simulation. Thus, we have explored methods for computing rates in the liquid phase. We have used relatively simply reactions and performed the studies for reactions in simple solvents; however, the approach can be extended to more complex systems of practical interests in energetic materials research.

The solvent effects on rates of chemical reactions have been extensively studied over the years. Much of the theoretical work is based on stochastic methods such as the Langevin theory. These methods allow for computations of rate constants without explicit consideration of the detailed dynamics of the solvent, and are thus powerful for treating complex systems where full-dimensional dynamical calculations are too costly. For instance, in the Langevin theory, the solvent influence on the reacting particle is modeled by a random fluctuating force and a friction kernel. Although these stochastic methods are useful for qualitatively understanding reactions in condensed phases, rate constants cannot be directly obtained for a given realistic system because quantities involved in the models concerning the solvent effects are generally unknown and must be determined by examining the detailed dynamics of the system. Molecular dynamics (MD) simulations provide a useful means for realistically modeling detailed dynamics and elucidating reaction mechanisms. However, a full-dimensional MD study is computationally expensive and may not be feasible for complex systems. An alternative approach is to map the real system to a stochastic model by performing a few MD calculations to determine the fitting parameters in the model. We have explored such an approach.

The basic idea is that the reacting molecule is subjected to random collisions with a mean frequency α. Between collisions, the dynamics of the molecule is governed solely by the equations of motion for the molecule itself. The effects of the solvent are modeled by random collisions. Under the strong collision assumption, the velocities of the molecule are randomized after each collision by sampling from the Boltzmann distribution while the coordinates are held fixed. Since only the motion of the molecule is explicitly treated, the method is far less costly than full-dimensional MD simulations. The parameter used to model the solvent effects is the collision frequency α, which is related to the liquid density ρ of the system. There have been studies where both MD simulations and the stochastic dynamics method were employed on the same system; but no attempt, to our knowledge, had previously been made to quantitatively relate α and ρ for any system.

We first investigated this idea with an application to *cis-trans* isomerization in HONO, which is one of the simplest molecules that exhibit *cis-trans* isomerization and one that has been extensively studied experimentally and theoretically. We used a model system with a HONO molecule embedded in liquid krypton and performed MD simulations to obtain isomerization

rates at several liquid densities. We also computed rate constants using the stochastic dynamics method for a wide range of collision frequencies α for these two sets of computed rates. We then examine the relationship between the liquid density ρ and the collision frequency α. Comparisons of the two sets of the computed rates show that for a wide range of liquid densities there is a simple linear relation between the liquid density ρ and the collision frequency α, that is, $\alpha = c\rho$. This suggests that once the constant c is determined from a molecular dynamics calculation at a single density, the reaction rates can be obtained from stochastic dynamics calculations for the entire range of liquid densities where $\alpha = c\rho$ holds. The applicability of the combined molecular dynamics and stochastic dynamics approach provides a practical means for obtaining rate constants at considerable savings of computer time compared to that required by using full-dimensional molecular dynamics simulations alone. The results of this work have been published.[7] Given the success of this study, we next carried out a similar study of bond fission in HONO (i.e., HONO → OH + NO).

Intuitively, the solvent effects on dissociation reactions should be different from those for isomerizations; the cage effect due to the solvent that forces recombination should be a prominent factor in dissociation reactions. Thus, the relation between α and ρ as well as the dependence of the reaction rate on ρ are expected to be different from that for isomerization. To establish the relation between α and ρ, we have performed two sets of calculations. We calculated the rate as a function of α using the stochastic dynamics method. We also calculated the rate at four liquid densities by using the full-dimensional MD simulations with a HONO molecule inside liquid Kr. The relation between α and ρ was found by pairing α and ρ that have the same rate. In our study of the *cis-trans* isomerization of HONO in liquid Kr, we found that α and ρ obey a simple linear relation, $\alpha = c\rho$. For the O-N bond dissociation of HONO in liquid Kr, we found that the relationship is more complicated, but is accurately described by an analytical expression. We have also found that the solvent effects are different for the isomerization and dissociation reactions. For isomerization the rate is in the low-collision regime and increases with increasing liquid density, whereas for dissociation the rate is in the high-collision regime and decreases with increasing liquid density. A manuscript has been submitted for publication.

In both cases, based on one MD simulation at a single density, the reaction rates can be obtained from stochastic dynamics for a wide range of liquid densities. The approach thus provides tremendous savings of computational time compared to full-dimensional MD simulations. The results to date show that the method is applicable to isomerization and dissociation reactions of small molecules in rare-gas liquids. In future work we will extend the studies to larger, more complicated systems, including more realistic energetic molecules and in reactions in neat liquids.

**Reaction Pathways for Unimolecular Dissociations of Energetic Molecules**
A major challenge to theoretical chemists and a particular need in energetic materials research is the development of methods for simulations and rate calculations for sequential, branching reactions. The practical problems range from soot formation to the decomposition of an energetic material such as RDX. We have long been interested in this problem within the context of unimolecular decomposition reactions. We are pursuing two lines of research that we expect to join when both are more mature. First, we are using quantum chemistry to explore the

transition states and intermediates in the chemical decomposition of energetic molecules. The other aspect of this work is purely developmental at this stage and focuses on methods for fitting ab initio potential energy surfaces and for performing direct dynamics simulations (a brief mention of this work is given below).

During this report period quantum chemistry studies of the decomposition pathways of 1,3,3-trinitroazetidine (TNAZ) and dimethylnitramine have been carried out. Possible decomposition transition-states, intermediates, and products of TNAZ were identified and the structures, energies, and vibrational frequencies were determined at the B3LYP/6-31G(d,p) level. Four major pathways are apparent. Two pathways are initiated by the fission of the N-NO$_2$ and C-NO$_2$ bonds to yield radical intermediates, while the other two pathways involve the molecular elimination of HONO. Energy profiles for the pathways and possible routes to some of the experimentally observed species of TNAZ decomposition have been determined. The energies required to initiate the NO$_2$ bond fission pathways are 4 to 8 kcal/mol lower than the HONO elimination pathways. In the gas phase, the NO$_2$ elimination pathways will be the dominant routes for TNAZ decomposition. In the condensed phase, however, this trend may be reversed. This work has been published: S. Alavi, L. M. Reilly, and D. L. Thompson, J. Chem. Phys. **119**, 8297 (2003).

Examination of the reported experimental and theoretical results from several researchers shows that there is an significant dispersion in the values of the Arrhenius parameters of the rate constants for the unimolecular decomposition of DMNA. The structures and energies of the reactant, intermediates, products, and transition states of the initial stages of DMNA decomposition of have been determined by quantum chemical calculations at several levels of theory. Kinetic parameters for these decomposition steps have been obtained using the RRKM formalism for the range 300-5000 K. The pathways considered are NO$_2$ elimination, HONO elimination, and NNO$_2$-NONO rearrangement. The NO$_2$ elimination channel is the main channel of gas phase decomposition of DMNA in the 300-5000 K range of temperatures. The HONO elimination channel has the next lowest decomposition energy but at high temperatures the nitro-nitrite rearrangement competes with it.

The rate constants as functions of temperature for NO$_2$ elimination, HONO elimination, and nitro-nitrite arrangement have been obtained from values of the energies and frequencies using RRKM theory; Arrhenius plots are shown in the figure below, where the curves are identified as follows: (---) NO$_2$ elimination, (—) HONO elimination, and (⋯) nitro-nitrite rearrangement.
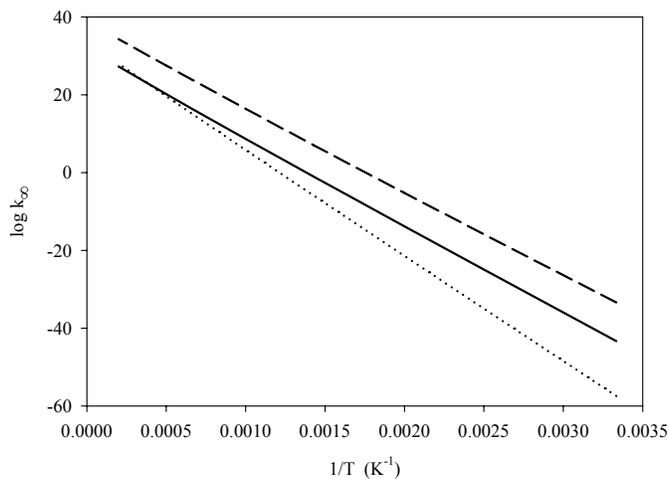
The Arrhenius parameters for NO_2 elimination are in good agreement with the values of previous theoretical studies. The HONO elimination channel has a lower value of the pre-exponential factor compared to NO_2 elimination because the transition state for the HONO elimination pathway is entropically unfavorable. Clearly, the NO_2 elimination is the main decomposition channel of DMNA in the range of 300-5000 K. The HONO elimination has a higher rate than the nitro-to-nitrite rearrangement but at high temperatures the rates of these two reactions becomes comparable. The experimental evidence is that the presence of NO in the DMNA decomposition products is due to the nitro-nitrite rearrangement followed by breaking of the weak NO-NO bond. Our results show that at low temperatures, this channel is the third in importance and becomes comparable with the HONO elimination channel only at higher temperatures.

An important part of predicting the behavior of energetic materials is better practical methods for computing the rates of chemical reactions. A critical problem is the formulation of PESs. For purely predictive methods it necessary that the PESs be based on quantum chemistry calculations, but this remains a major obstacle to applications to large polyatomic molecules and radicals. The most straightforward way to make use of *ab initio* results is to simply compute the forces "on the fly" during a simulation; however, the difficulty here is that studies are restricted to the lower-level quantum methods, which are often not sufficiently accurate for reliable predictions of rates. The common alternative to "direct dynamics" is to fit the *ab initio* energies to an analytical function, which allows for much more rapid evaluations of the forces during simulations as well as scaling of the *ab initio* results to correct for the inaccuracies inherent in a low-level theory. Fitting a global PES is extremely tedious and not readily generalizable, thus a huge investment of human labor is required in each case. Furthermore, the analytical forms are not sufficiently flexible to accurately fit the *ab initio* points. This was our motivation for suggesting, in the 1970's, that local fitting functions should be used to fit *ab initio* energies. We proposed using cubic splines, which provide the desired flexibility to yield accurate, smooth first and second derivatives but requires a fairly dense grid of *ab initio* points.[8] The modified Shepard methods suggested by Ischtwan and Collins[9] in 1994 are superior to cubic splines. They have combined surface fitting with MD simulations in an iterative scheme for successively and automatically improving the PES. This procedure selects the locations for additional *ab initio* calculations in regions of configuration space that are dynamically important. The procedure is simple and readily automated but gradients and Hessians, which are not readily available in the high-level *ab initio*, are required at every point. We have developed interpolative moving least-squares (IMLS) fitting procedures that promise to be more useful than other methods, mainly because it does not require derivatives.[10]

During this report period we began applications of the IMLS methods to reactions important in the decomposition of nitramines. We have begun with a study of the unimolecular decomposition of H_2CN, which is currently under study in Professor Paul Dagdigian's laboratory at Johns Hopkins. We are doing this work in collaboration with Drs. Larry Harding and Al Wagner at ANL. Ab initio energies have been fit and rates of dissociation are being carried out. These results are being generated in advance of Professor Dagdigian's measurements of the rates, thus they will be truly predictive. The immediate goal is to establish the accuracy of this

approach for a significant chemical reaction. We plan to extend the work to include bimolecular reactions of H_2CN with other radicals and small molecules.

Our goal is to develop software that manages the quantum chemistry calculations in direct response to the needs of a MD simulation to provide an *ab initio* prediction of a specified reaction rate. If successful, and the prospects are good, this could make MD studies of reactions a practical tool for all who are interested in reaction kinetics rather than a technique limited to use by experts.

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Plans: The following will be the focus of our group for the coming year:
- Continuation of studies of melting of energetic materials
- Further development of methods for rate calculations for condensed-phase reactions
- Refinement and applications of methods for fitting *ab initio* PESs for reactions
- Rate calculations and dynamics calculations for the chemical decomposition of energetic molecules
- Simulations of shocked solids and liquids

Personnel:

Ms. Lisa M. Riley (Graduate Student, Supported by MURI funds)
Dr. Paras M. Agrawal (Research Associate, Supported by MURI funds.)
Dr. Saman Alavi (Research Associate, Partially supported by MURI funds.)
Dr. Yin Guo (Research Associate, Partially supported by MURI funds.)

Publications:
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Books: (1)
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Faculty Supported: (9)
     John Adams
     Herman Ammon
     Rodney Bartlett
     Donald W. Brenner
     David Ceperley
     Chistopher J. Cramer
     Richard Martin
     Donald L. Thompson
     Donald G. Truhlar

Graduate Students Supported: (14)
     Ed Wells
     William Mattson
     Edward Bukhman
     Lisa M. Riley
     DeCarlos Taylor
     Tom Henderson
     Anthony Yau
     Josh McClellan
     Tom Hughes
     Luis Galiano
     Stacie Gregory
     Ali Siavosh-Haghighi
     Jason D. Thompson
     Tomas Szabo

Postdoctoral Fellows Supported: (5)
     Zuyue Du
     Simone Chiesa
     Paras M. Agrawal
     Saman Alavi
     Yin Guo

Other Research Staff: (2)
     Sayta Prasad, sabbatical associate (Physics, Ranchi Univ, India)
     Xinlu Chen (visiting professor)
     Kai Wang (senior researcher)

Undergraduate Students Supported: (1)
     Nicole Dueker

PhDs Awarded:
W. D. Mattson, thesis, University of Illinois, 2003.

Substantial Interactions with DoD and Other Researchers:
Dr. Betsy Rice (ARL)
Dr. Ed Byrd (ARL)
Dr.William Mattson (ARL)
Dr. Alfred Stern (NAVSEA, Indian Head, MD)
Dr. Willam Koppes (NAVSEA, Indian Head, MD)
Dr. Rao Surapaneni (Picatinny Arsenal)
Dr. Paritosh Dave (Picatinny Arsenal)
Dr. Robert Chapman (NAWC, China Lake, CA)
Dr. Philip Eaton (Univ. of Chicago)
Dr. Harold Shechter (The Ohio State Univ.)
Dr. Steve Bunte (ARL)
Dr. Shashi Karna (ARL)
Dr. Cary Chabalowski (ARL)