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14. ABSTRACT We have performed fundamental experimental and theoretical studies of insensitive energetic materials (FOX 7, HMX, RDX, TATB and PETN) with the aim of better-ascertaining their behavior under extreme conditions as well as seeking to understand more about what makes them relatively stable in the hope of designing better explosives in the future. We have also developed novel methods to study these important materials which we feel will aid future studies of insensitive munitions.					
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Effect of Defects on Mechanisms of Initiation and Energy Release in Energetic Molecular Crystals: Final Report

ABSTRACT

We have performed fundamental experimental and theoretical studies of insensitive energetic materials (FOX 7, HMX, RDX, TATB and PETN) with the aim of better-ascertaining their behavior under extreme conditions as well as seeking to understand more about what makes them relatively stable in the hope of designing better explosives in the future. We have also developed novel methods to study these important materials which we feel will aid future studies of insensitive munitions.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1. Skryl, Y. and Kuklja, M.M., "Diffusion of Point Defects in Shocked Molecular Crystals, Phys. Rev. B 71 (2005) 094109.
2. J.Slutsker, J., Thornton, K., Roytburd, A.L., Warren, J.A., and McFadden, G.B., "Phase field modeling of solidification under stress," Phys.Rev. B 74 (2006) 014103.
3. Zerilli, F.J., and Kuklja, M.M., "First Principles Calculation of the Mechanical Compression of Two Organic Molecular Crystals," J Phys. Chem A 110 5173-5179.
4. Skryl, Y. and Kuklja, M.M., "Diffusion of Point Defects in Shocked Molecular Crystals, Phys. Rev. B 71 (2005) 094109.
5. J.Slutsker, J., Thornton, K., Roytburd, A.L., Warren, J.A., and McFadden, G.B., "Phase field modeling of solidification under stress," Phys. Rev. B 74 (2006) 014103.
6. Zerilli, F.J., and Kuklja, M.M., "First Principles Calculation of the Mechanical Compression of Two Organic Molecular Crystals," J Phys. Chem A 110 5173-5179.
7. Kimmel, A.V.; Sushko, P.V.; Shluger, A.L.; and Kuklja, M.M., "Effect of charged and excited states on the decomposition of 1,1-diamino-2,2-dinitroethylene molecules," J. Chem. Phys. 126 (2007) 234711/1-10.
8. Kuklja, M.M., and Rashkeev, S.N., "Shear-strain-induced chemical reactivity of layered molecular crystals," Appl. Phys. Lett. 90 (2007) 151913/1-3.
9. Kuklja, M.M. and Rashkeev, S.N., "Shear-strain-induced structural and electronic modifications of the molecular crystal 1,1-diamino-2,2-dinitroethylene: Slip-plane flow and band gap relaxation," Phys. Rev. B 75 (2007) 104111/1-10.
10. Kuklja, M.M., Rashkeev, S.N., and Zerilli, F.J., "Shear-strain induced decomposition of 1,1-diamino-2,2-dinitroethylene," Appl. Phys. Lett. 89 (2006) 071904/1-3.
11. Slutsker, J., Thornton, K., Roytburd, A.L., J.A.Warren, J.A., and McFadden, G.B., "Phase field modeling of solidification under stress", Phys. Rev. B 74 (2006) 014103.
12. Zerilli, F.J. Hooper, J.P., Kuklja, M.M., "Ab initio studies of crystalline nitromethane under high pressure," J. Chem. Phys. 126 (2007) 114701/1-8.
13. Zerilli, F.J., Kuklja, M.M., "Ab Initio Equation of State of an Organic Molecular Crystal: 1,1-Diamino-2,2-dinitroethylene," J. Phys. Chem. A 111 (2007) 1721-1725.
14. O. Tschauner, B. Kiefer, and Y. Lee, M. Pravica, M. Nicol, and E. Kim, "Structural transition of PETN-1 to ferroelastic orthorhombic phase PETN-III at elevated pressures," J. Chem. Phys. 1278 (2007) 094502/1-5.
15. M. Pravica, B. Yulga, Z Liu, and O. Tschauner, "Infrared study of 1,3,5-triamino-2,4,6-trinitrobenzene under high pressure," Phys. Rev. B 76 (2007) 064102/1-4.
16. Y. Skryl, A.A. Belak, and M.M. Kukla, "Shock-induced polarization in distilled water," Phys Rev. B (2007) 064107/1-9.
17. A.V. Kimmel, P.V. Sushko, A.L. Shluger, and M.M. Kukla, "The effect of molecular and lattice structure on hydrogen transfer in molecular crystals of diamino-dinitroethylene and triamino-trinitrobenzene," J. Phys. Chem. A, 112 (2008) 4496-4500.
18. M.W. Conroy, I.I. Oleynik, S.V. Zybin, and C.T. White, "First-principles investigation of anisotropic constitutive relationships in pentaerythritol tetranitrate," Phys. Rev. B 77 (2008) 094107/1-8.
19. H. Giefers and M. Pravica, "Radiation-Induced Decomposition of PETN and TATB under Extreme Conditions," J. Phys. Chem. A 112, (2008) 3352.
20. A. Lagutchev, S. A. Hambir and D. D. Dlott, "Nonresonant Background Suppression in Broadband Vibrational Sum-Frequency

Generation Spectroscopy," J. Phys. Chem. C 111 (2007) 13645-13647.

21. Z. Wang, D. G. Cahill, J. A. Carter, Y. K. Koh, A. Lagutchev, N.-H. Seong and D. D. Dlott, "Ultrafast dynamics of heat flow across molecules," Chemical Physics 350, 31-44 (2008).
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28. A.V.Kimmel, P.V.Sushko, A.L.Shluger, and M.M.Kuklja, The effect of molecular and lattice structure on hydrogen transfer in molecular crystals diamino-dinitroethylene and triamino-trinitrobenzene, J. Phys. Chem. A 112 (19), 4496-4450 (2008).
29. Maija M. Kuklja and Sergey N. Rashkeev, Modeling of defect induced phenomena in energetic materials, book chapter in Hydrostatic Compression of Energetic Materials, editors: S. Peiris and G. Piermarini, Springer-Verlag, Chapter 8, pp. 322-361 (2008).
30. "High-pressure far- and mid-infrared study of 1,3,5,7 Triaminotrinitrobenzene," M. Pravica, B. Yulga, S. Tkachev, Z. Liu, Journal of Physical Chemistry A 113 (32), pp. 9133-9137 (2009).
31. Maija M. Kuklja and Sergey N. Rashkeev, "Interplay of decomposition mechanisms at shear-strain interface," J. Phys. Chem. C (letters), 113 (1), 17-20 (2009).
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35. Maija M. Kuklja and Sergey N. Rashkeev, "Interplay of decomposition mechanisms at shear-strain interface," J. Phys. Chem. C (letters), 113 (1), 17-20 (2009).
36. Maija M. Kuklja and Sergey N. Rashkeev, "Molecular mechanisms of Shear-strain Sensitivity of Energetic Crystals DADNE and TATB," Invited paper to appear in JEM, 28, 1-12, 2010.
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46. A.C. Landerville, M.W. Conroy, I.I. Oleynik, and C.T. White, "Prediction of isothermal equation of state of an explosive nitrate ester by van der Waals density functional theory" J. Phys. Chem. Lett. 1, 346, (2010).
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50. M. Pravica, M. Galley, E. Kim, P. Weck, and Z. Liu, "A Far- and Mid- Infrared Study of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) under High Pressure," , Chemical Physics Letters 500, pp. 28-34 (2010).

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Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

1. Conroy, M., Oleynik, I., and White, C., "First-principles modeling of energetic materials," American Physical Society, Baltimore, March 2006.
2. Giefers, H., Pravica, M., Yulga, B., Romano, E., and Nicol, M., "Radiation-induced Decomposition of PETN and TATB," Gordon Research Conference on Energetic Materials Poster Session, "Tilton, NH, June 2006.
3. Giefers, H., Pravica, M., Yulga, B., Romano, E., and Nicol, M., "Synchrotron Radiation-induced Decomposition of Explosives at High Pressure," Gordon Research Conference on Research at High Pressures Poster Session, "Biddeford, ME, June 2006.
4. Giefers, H., Pravica, M., Yulga, B., Romano, E., and Nicol, M., "Radiation-induced Damage of Explosives at Ambient and High Pressures," American Crystallographic Association, Honolulu, July 2006.
5. Gobin, C., Orwig, J., and Nicol, M., "High-Pressure Synchrotron Radiation X-Ray Diffraction and Vibrational Spectroscopic Studies of 3,3,7,7 tetrakis (difluoramino) octahydro-1,5-dinitro-1,5-diazocine (HNFX)," American Physical Society, March 2006.
6. Kukla, M., "Defect-induced phenomena in explosive solids", (Invited lecture) Seminar series, Materials Research Laboratory, University of California, Santa Barbara, September, 2005.
7. Kukla, M., "Materials Research and Education: Perspectives and Challenges, Modeling of organic crystals containing defects", (Invited), NSF Division of Materials Research Seminar Series, November, 2005.
8. Kuklja, M.M., "Defect-Induced Phenomena in Shocked Energetic Solids," (Invited, not delivered), International Conference on New Models and Hydrocodes for Shock Wave Processes in Condensed Matter, Dijon, France, April, 2006.
9. Kuklja, M.M., "Effect of Defects on Mechanisms of Initiation and Energy Release in Energetic Molecular Crystals," (Invited), UNLV, Las Vegas, May 2006.
10. Pravica, M., "High Pressure Studies of Explosives and Metals," East Carolina University, Greenville, March 2006.
11. Roytburd, A.L., "Understanding Martensite," (Invited) International Conference on Solid-Solid Phase Transformations, Phoenix, May 2005.
12. Yu, Y., and Oleynik, I., "Interatomic bond-order potentials for atomistic simulations of materials at extreme conditions," American Physical Society, Baltimore, March 2006.
13. Zerilli, F., Hooper, J., and Kukla, M., "Ab Initio Studies of High Pressure States of Crystalline Nitromethane," American Physical Society, Baltimore, March 2006.
14. Zerilli, F.J., Hooper, J.P. Hooper, and Kuklja, M.M., "Ab Initio Studies of High Pressure States of Crystalline Nitromethane," International Conference on New Models and Hydrocodes for Shock Wave Processes in Condensed Matter, Dijon, France, April, 2006.
15. Kuklja, M.M., "Defect-induced phenomena in energetic molecular crystals," Invited seminar, University College London, London, UK, September, 2006
16. Kuklja, M.M., "Shear-triggered decomposition in energetic materials: ab initio study," Invited seminar within Physics Distinguished Speaker Colloquium, Virginia Tech, Blacksburg, September 2006.
17. Kuklja, M.M., "Defect-induced decomposition in energetic materials: ab initio study," Invited seminar CCNY, New York, September 2006.
18. Kuklja, M.M., "First-principles modeling of defect-induced decomposition in shocked energetic materials," Invited seminar within Materials Science and Engineering Distinguished Lecturer series, University of Maryland, College Park, MD October 2006.
19. Kuklja, M.M., "Towards energetic materials by design: Ab initio study of organic molecular crystals." Invited Lecture at Materials Science and Engineering Department Colloquium, University of Michigan, Ann Arbor, MI, January, 2007.

20. Kuklja, M.M., "Ab initio study of shear-strain induced chemistry in energetic materials," Invited talk at Work In Progress seminar series, Lawrence Livermore National Laboratory, Livermore, CA, February, 2007.
21. Nicol, M., Gobin, C., and Kim, E., "Vibrational spectra of solid HNFx (C₆H₈F₈N₈O₄): Experiments and theory," American Physical Society, Denver, CO, March 2007. <http://meetings.aps.org/link/BAPS.2007.MAR.V23>.
22. Nicol, M., "Diffraction, Explosives, and Dynamics at High Pressures, COMPRESS Annual Meeting, Lake Morey, VT, June 2007. (Invited plenary talk.).
23. Oleynik, I., "First-principles Modeling of Energetic Materials: Challenges and Opportunities," Gordon Research Conference on Energetic Materials, Tilton, NH, June 2006. (Invited talk).
24. Pravica, M., "High Pressure and High Temperature Decomposition Studies of PETN and TATB," American Physical Society, Denver, CO, March 2007.
25. Rashkeev, S., and Kuklja, M., "Shear strain induced structural and electronic modifications of the energetic molecular crystal 1,1-diamino-2,2-dinitroethylene," American Physical Society, Denver, CO, March 2007.: <http://meetings.aps.org/link/BAPS.2007.MAR.V23.4>
26. Roytburd, A.L., "Elastic Domains in Martensitic Transformations", Invited Talk on International Conference on Phase Transformations and Strength of Solids, Chernogolovka, Moscow Region, September 2006.
27. Yulga, B., Pravica, M., Liu, Z., Tschauner, O., and Nicol, M., "An Infrared Study of Secondary Explosives under High Pressure," American Physical Society, Denver, CO, March 2007. <http://meetings.aps.org/link/BAPS.2007.MAR.V23>.
28. Landerville, A., Oleynik, I., and White, C., "First-principles molecular reactive dynamics of energetic materials," American Physical Society, Denver, CO, March 2007. <http://meetings.aps.org/link/BAPS.2007.MAR.B21.7>
29. McLaughlin, K., Ladanov, M., Oleynik, I., Zybin, S., Elert, M., and White, C.T., "Anomalous elastic response of diamond single crystals to shock compression," American Physical Society, Denver, CO, March 2007. <http://meetings.aps.org/link/BAPS.2007.MAR.B21.3>.
30. A.V. Kimmel, P.V. Sushko, A.L. Shluger, and M.M. Kukla, "Multi-scale approach for modelling structural and electronic defects in energetic materials," EPSRC Network Meeting on Condensed phase reactive flow, Cambridge, UK, September, 2007.
31. Maija M. Kukla, "Modeling Molecular Materials: from Molecules to Complexity," Invited talk Accelrys, Cambridge, UK, October 2007.
32. I.I. Oleynik, "Interatomic Bond-Order Potentials for Atomistic Simulations of Materials at Extreme Conditions," 59th Southeast Regional Meeting, American Chemical Society, Greenville, SC, October 2007.
33. Maija M. Kukla, Modeling Molecular Materials: from Molecules to Complexity, Invited talk at the distinguished speaker series, Yeshiva University, NY, November, 2007.
34. Maija M. Kukla, Modeling Molecular Materials: from Molecules to Complexity, Invited talk at the distinguished speaker series, Jackson State University, MS, November, 2007.
35. Maija M. Kukla, Modeling High Explosive Materials: from Structure of Molecules to Complexity of Detonation Mechanisms, Invited talk at the distinguished speaker series, Naval Surface Warfare Center-Indian Head Division, Indian Head, MD, December, 2007.
36. A.V.Kimmel and M.M.Kukla, Chemical reactions in crystalline FOX-7: H transfer, C-NO₂ bond fission, and CONO-isomerization, Condensed Matter group meeting, Physics Department, University College London, London, UK, December, 2007.
37. Maija M. Kukla, Force Fields – ReaxFF, AIREBO, and nonreactive force fields, Discussion leader, ARO MURI Workshop Insensitive Munitions, UNLV, Las Vegas, February, 2008.

38. M. Pravica, B. Yulga, S. Tkachev, and Z. Liu. "High Pressure Studies of TATB,".Poster, NNSA-SSAA, Washington, DC, February 2008.
39. B. Yulga, "Static high pressure spectroscopic studies on energetic materials," Research Seminar at the Los Alamos National Laboratory, May 2008.
40. Maija M. Kukla and Sergey N. Rashkeev, "Molecular Mechanisms of Shear-strain Sensitivity of Energetic Crystals," Invited Lecture at New Models and Hydrocodes for Shock Wave Processes in Condensed Matter, Lisbon, Portugal, May, 2008.
41. A.V. Kimmel, P.V. Sushko, A.L. Shluger, and M.M. Kukla, "Structure and Properties of Stereo Isomer Defects in DADNE," New Models and Hydrocodes for Shock Wave Processes in Condensed Matter, Lisbon, Portugal, May, 2008.
42. Maija M. Kukla, "Mechanisms of Initiation of Detonation at Micro-scale," Invited Lecture at discussion section, Discussion Leader, New Models and Hydrocodes for Shock Wave Processes in Condensed Matter, Lisbon, Portugal, May, 2008.
43. B. Yulga, S. Tkachev, M. Pravica, Z. Liu, "Static High Pressure Vibrational Spectroscopic Studies of TATB," Poster at Gordon Research Conference on Energetic Materials, Tilton, NH, June 2008.
44. Michael Pravica, invited talk to Los Alamos National Laboratory (DE-9) entitled: "Studies of hydrocarbons, energetic materials, and wide bandgap materials under extreme conditions," Los Alamos, NM 7/22/09.
45. Michael Pravica, invited talk for the HiPSEC review: "Studies of hydrocarbons, energetic materials, and wide bandgap materials under extreme conditions," Las Vegas, NV 5/11/09.
46. Malcolm F. Nicol, invited talk for the MURI review, Columbia Mo, January 2009.
47. Martin Galley, Sergey Tkachev, Michael Pravica, Contributed poster: "Raman Studies of 1,3,5,7 Cyclooctatetraene at High Pressure," NSF REU presentation, Las Vegas, NV (8/08).
48. Edward Romano, contributed talk: "Raman spectrum of 1,3,5,7-cyclooctatetraene as a function of pressure," American Physical Society, California Section Meeting, Cal State University Dominguez.Hills, October 17-18, 2008.
49. Brian Yulga, contributed talk: "Static high pressure infrared spectroscopic studies on triamino-trinitro-benzene (TATB)," , American Physical Society, California Section Meeting, Cal State University Dominguez Hills, October 17-18, 2008.
50. Sergey N. Tkachev, contributed talk: "High Pressure Studies of 1,3,5,7-Cyclooctatetraene and Cyclopentane: Experiment and Theory," , American Chemical Society (ACS) 42nd Western Regional Meeting, Las Vegas, NV, 9/26/08.
51. Maija M. Kuklja, Embedded Cluster Model for simulation of energetic materials containing defects, ARO MURI Workshop Insensitive Munitions, University of Missouri Columbia, Columbia, Missouri, January, 2009.
52. Maija M. Kuklja and Sergey Rashkeev, Mechanisms of Initiation of Detonation at Micro-scale in DADNE and TATB, ARO MURI.Workshop Insensitive Munitions, University of Missouri Columbia, Columbia, Missouri, January, 2009.
53. Maija M.Kuklja, Compression and Shear-strain Induced Processes in Energetic Molecular Crystals, Invited lecture at "The Changing Face of Chemistry in the 21st Century," 42nd Western Regional Meeting of the American Chemical Society, September 2008.
54. Michael Pravica, Presented poster at the Gordon Research Conference "Energetic Materials," in Tilton, NH entitled, "High pressure studies of HMX," 6/16/10.
55. Michael Pravica (invited) Challenges in Compression Science Workshop talk entitled: "Future Desired Directions in Static High Pressure Science," Santa Fe, NM 9/24/09.
56. Dana Dlott,(invited) 21st Century Needs and Challenges of Compression Science Workshop, , "Shock compression of molecules with high time and space resolution" Santa Fe, NM, Sept. 2009.

57. Dana Dlott (invited) Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) annual meeting, "Vibrational energy in molecules studied with 2D vibrational sum-frequency generation" Louisville, KY, Oct. 2009.
58. Dana Dlott (invited), "Vibrational energy in materials with high time and space resolution," North Carolina State University, Jan. 2010.
59. Dana Dlott (invited) Army Research Office Review of Nano-engineered energetic materials, , "Ultrafast dynamics of NEEMs," Aberdeen, MD, Mar. 2010.
60. Dana Dlott (invited) American Chemical Society Annual Meeting, "Vibrational Energy in Molecules with High Time and Space Resolution" San Francisco, CA Mar. 2010.
61. Dana Dlott (invited) Northwestern University Department of Chemistry, , "Vibrational Energy with High Time and Space Resolution," Evanston, IL Mar. 2010.
62. Dana Dlott, NATO Munitions Safety Information Analysis Center (MSIAC) Workshop on Insensitive Energetic Materials, Nato Headquarters, "Molecular mechanisms of insensitive explosives," Brussels, Belgium, May 2010.
63. Dana Dlott (invited), Molecular Dynamics Contractors' Meeting, Air Force Office of Scientific Research, , "Time resolved spectroscopy of molecules at interfaces," Chantilly, VA, May 2010.
64. Dana Dlott (invited) Army Research Office Symposium on Insensitive Energetic Materials, "Fundamental Processes and Properties of Insensitive Energetic Materials," Aberdeen, MD, June 2010.
65. Dana Dlott: (invited, plenary), "Vibrational energy in molecules with high time and space resolution", International Conference on Raman Spectroscopy (ICORS X), Boston, MA, Aug. 2010.
66. Dana Dlott (invited) "Ultrafast Dynamics of Impact Chemistry: Initiation to Detonation", Aug. 2010, Joint JSF-IAS Workshop on Interface Physics Singapore August 29-September 5, 2010.
67. Neelanjana Bhattacharya, "X-Ray Raman scattering of Aluminum Nitride under high pressure," 2010 Annual Meeting of the California-Nevada Section of the APS, Pasadena, CA, October 29, 2010. <http://meetings.aps.org/Meeting/CAL10/Event/135907>
68. Martin Galley, "Studies of Melamine Under Extreme Conditions," 2010 Annual Meeting of the California-Nevada Section of the APS, Pasadena, CA, October 29, 2010. <http://meetings.aps.org/Meeting/CAL10/Event/135905>
69. Michael Pravica, "A Far- and Mid-Infrared Study of HMX (octahydro- 1,3,5,7-tetranitro-1,3,5,7-tetrazocine) under High Pressure," 2010 Annual Meeting of the California-Nevada Section of the APS, Pasadena, CA, October 29, 2010. <http://meetings.aps.org/Meeting/CAL10/Event/135866>

Number of Presentations: 69.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

1. Zerilli, F.J., and Kuklja, M.M., "Thermodynamic Properties of Organic Molecular Crystals from First Principles," in E. Dingus, ed., Proceedings Joint 20th AIRAPT and 43rd EHPRG International Conference on High Pressure Science and Technology (Forschungszentrum Karlsruhe GmbH, Karlsruhe, 2005).
2. A.V. Kimmel, P.V. Sushko, A.L. Shluger, and M.M. Kukla, "Decomposition chemistry of crystalline DADNE," New Trends in Research of Energetic Materials proceedings, Pardubice, Czech Republic, p.199 (2008).
3. A.V. Kimmel, P.V. Sushko, A.L. Shluger, and M.M. Kukla, "Charge and excitation-triggered decomposition of DADNE," 17th DYMAT Technical Meeting Proceedings, The High Rate Mechanical Properties of Energetic Materials, their Binders or Simulants, Cavendish Laboratory University of Cambridge, UK, 35, (2007).

Peer-Reviewed Conference Proceeding publications (other than abstracts):

1. Kuklja, M.M., Rashkeev, S., and Zerilli, F., "The atomic and electronic structure of defects in 1,1-diamino-2,2-dinitroethylene," in Furnish, M., ed., Shock Compression of Condensed Matter – 2005 (Amer. Inst. Phys. Conf. Proc. 845, New York, 2006) pp. 535-538.
2. Skryl, Y., Belak, A.A., and Kuklja, M.M., "Numerical Simulation of Shock-Induced Polarization in Binary Electrolytes," in Furnish, M., ed., Shock Compression of Condensed Matter – 2005 (Amer. Inst. Phys. Conf. Proc. 845, New York, 2006) pp. 355-358.
3. Zerilli, F.J., and Kuklja, M.M., "Equation of State of 1,1-diamino-2,2-dinitroethylene from First Principles," in Furnish, M., ed., Shock Compression of Condensed Matter – 2005 (Amer. Inst. Physics Conf. Proc. 845, New York, 2006), pp. 183-186.
4. Michael Pravica, Zachary Quine, Edward Romano, Sean Bajar, Brian Yulga, Wenge Yang, Daniel Hooks, "Anisotropic decomposition of energetic materials," APS Shock Compression of Condensed Matter (SCCM) Conference Proceedings CP955 (2007).
5. M. Conroy, I.I. Oleynik, S.V. Zybin, and C.T. White, "Anisotropic constitutive relationships in energetic materials: PETN and HMX," SCCM-2007: AIP Conference Proceedings, 955, Editors: M. L. Elert, M. D. Furnish, R. Chau, N. Holmes, J. Nguyen 361-364 (2007).
6. A.V. Kimmel, P.V. Sushko, A.L. Shluger, and M.M. Kukla, An effect of charged and excited states on the decomposition of 1,1-diamino-2,2-dinitroethylene, SCCM-2007: AIP Conference Proceedings, 955, Editors: M. L. Elert, M. D. Furnish, R. Chau, N. Holmes, J. Nguyen, 389-392 (2007).
7. A. Landerville, I.I. Oleynik, M.A. Kozhushner, and C.T. White, "First-principles reactive molecular dynamics of chemistry in detonating energetic materials," SCCM-2007: AIP Conference Proceedings, 955, Editors: M. L. Elert, M. D. Furnish, R. Chau, N. Holmes, J. Nguyen 447-450 (2007).
8. K. McLaughlin, I.I. Oleynik, S.V. Zybin, M.L. Elert, and C.T. White, "Molecular dynamics simulations of an anomalous response of diamond to shock compression," SCCM-2007: AIP Conference Proceedings, 955, Editors: M. L. Elert, M. D. Furnish, R. Chau, N. Holmes, J. Nguyen 321-324 (2007).
9. I.I. Oleynik, M. Conroy, and C.T. White, "Anisotropic constitutive relationships in energetic materials: nitromethane and RDX," SCCM-2007: AIP Conference Proceedings, 955, Editors: M. L. Elert, M. D. Furnish, R. Chau, N. Holmes, J. Nguyen 401-404 (2007).
10. F.J. Zerilli and M.M. Kukla, "Ab Initio Equation of State for β -HMX," SCCM-2007: AIP Conference Proceedings, 955, Editors: M. L. Elert, M. D. Furnish, R. Chau, N. Holmes, J. Nguyen, 437-440 (2007).
11. J. A. Carter, Z. Wang, and D.D. Dlott (Invited paper) "Watching vibrational energy in molecules with high time and space resolution," in Proceedings of the XXist International Conference on Raman Spectroscopy, edited by R. Withnall and B.Z. Chowdhry (IM Publications LLP, Charlton, Chichester), pp. 469-470 (2008).
12. Maija M. Kuklja and Sergey N. Rashkeev, "Molecular instability at the shear-stress interface," 18th DYMAT Technical Meeting Proceedings, Cavendish Laboratory University of Cambridge, UK, 35, (2009).
13. M. Pravica, E. Romano, S. Tkachev and Z. Liu, "High pressure infrared study of 1,3,5,7-cyclooctatetraene (COT)," AIRAPT conference proceedings, Joint AIRAPT & HPCJ-50, Journal of Physics: Conferences Series 215, 012050 (2010).
14. Onise Sharia and Maija M. Kuklja, "Effect of defects on initiation of chemistry in HMX," in Shock Compression of Condensed Matter - 2009, edited by M.L.Elert, W.T.Buttler, M.D.Furnish, W.W.Anderson, and W.G.Proud, AIP conference proceedings 1195, (American Institute of Physics, Melville, New York, 2009), p.353-356.
15. Maija M. Kuklja and Sergey N. Rashkeev, "Autocatalytic decomposition at shear-strain interfaces," in Shock Compression of Condensed Matter - 2009, edited by M.L.Elert, W.T.Buttler, M.D.Furnish, W.W.Anderson, and W.G.Proud, AIP conference proceedings 1195, (American Institute of Physics, Melville, New York, 2009), p.365-368.
16. L.Wang, M.Kuklja, "Oxidation phase diagram of small aluminum clusters based on first-principles calculations," in Shock Compression of Condensed Matter - 2009, edited by M.L.Elert, W.T.Buttler, M.D.Furnish, W.W.Anderson, and W.G.Proud, AIP conference proceedings 1195, (American Institute of Physics, Melville, New York, 2009), p.773-776.
17. Lagutchev, A., Brown, K. E., Carter, J. A., Fu, Y., Fujiwara, H., Wang, Z., and Dlott, D. D., "Ultrafast vibrational spectroscopy of shock compression with molecular resolution," AIP Conference Proceedings 1195, 301-304 (2010).

18. Landerville, I.I. Oleynik, and C.T. White, “First-principles investigation of reactive molecular dynamics in detonating RDX and TATB”, AIP Conference proceedings Shock Compression of Condensed Matter -2009, 1195, 817 (2009).

19. M. Budzevich, M. Conroy, A. Landerville, Y. Lin , I.I. Oleynik, and C.T. White, “Hydrostatic equation of state and anisotropic constitutive relationships in 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)”, AIP Conference proceedings Shock Compression of Condensed Matter -2009, 1195, 545 (2009).

20. M. Conroy, M. Budzevich, A. Landerville, Y. Lin , I.I. Oleynik, and C.T. White, “Application of van der waals density functional theory to study physical properties of energetic materials”, AIP Conference proceedings Shock Compression of Condensed Matter -2009, 1195, 805 (2009).

21. Landerville, I.I. Oleynik, and C.T. White, “Reactive molecular dynamics of detonating PETN,” AIP Conference proceedings Shock Compression of Condensed Matter -2009, 1195, 813 (2009).

22. M. Conroy, A. Landerville, I.I. Oleynik, and C.T. White, “First-principles studies of hydrostatic and uniaxial compression of a new energetic material – an energetic nitrate ester”, AIP Conference proceedings Shock Compression of Condensed Matter -2009, 1195, 482 (2009).

23. X. Gu, Y. Lin, I.I. Oleynik, and C.T. White, “Molecular dynamics simulations of shock-induced defect healing in silicon”, AIP Conference proceedings Shock Compression of Condensed Matter -2009, 1195, 793 (2009).

24. Y. Lin, M. Budzevich, A. Landerville, I.I. Oleynik, and C.T. White, “Physical and chemical properties of a new energetic material Si-PETN,” AIP Conference proceedings Shock Compression of Condensed Matter -2009, 1195, 482 (2009).

25. “A High Pressure, High Temperature Study of 1,1 Diamino–2,2 Dinitro ethylene.,” M. Pravica, M. Galley, C. Park, High Pressure Research EHPRG 2010 conference proceedings, pp. 1-6 (2010).

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

25

(d) Manuscripts

1. “A High Pressure and High Temperature Study of Melamine,” submitted to the DIAMOND 2010 conference proceedings in Diamond and Related Materials (2010).

2. "High Pressure X-ray Raman Spectroscopic Study of Aluminum Nitride," submitted to Diamond and Related Materials(2010).

Number of Manuscripts:

2.00

Patents Submitted

Patents Awarded

Awards

1. UNLV College of Sciences Distinguished Researcher Award, College of Sciences, 2007, Malcolm F. Nicol

2. Zachary Quine (UNLV undergraduate physics major) received the Outstanding Graduate award from UNLV (December 2007).
3. Zachary Quine (UNLV undergraduate physics major) received a SMART fellowship to attend Princeton for his Ph.D. studies in chemistry after working for one year at the ARL, Aberdeen Proving Grounds with Dr. Kevin McNesby.
4. Prof. Oleynik was promoted to Associate Professor at University of South Florid and awarded tenure.
5. Prof. Pravica was promoted to Associate Professor at the University of Nevada, Las Vegas and awarded tenure in 2008
6. Jefferey A. Carter received a Merck Fellowship in Physical or Analytic Chemistry
7. Dana D. Dlott was promoted to Lycan Professor of Chemistry
8. Yuanxi Fu was awarded the University of Illinois Urbana Champaign Department of Chemistry fellowship
9. Kathryn E. Brown was awarded the University of Illinois Urbana Champaign Department of Chemistry fellowship.
10. M. Kukla, Nominating Committee Chair, APS Shock Compression of Condensed Matter Executive Committee (2009-12)
11. M. Kukla, Embassy Science Fellow, (May-July, 2010), US Embassy in Moscow, Russian Federation, Science Consultant to the US Government upon request of the State Department, M. Kukla served on numerous international advisory boards.
12. Aaron Landerville has been awarded the USF Outstanding Graduate Student award in Spring 2010 for his outstanding research in energetic materials
13. Michael Conroy has been awarded the USF Best Dissertation award and has been nominated for National Best Dissertation award in Spring 2010 for his PhD dissertation "Density Functional Theory Studies of Energetic Materials"
14. Michael Conroy has been awarded NRC Postdoctoral Research Associateship to continue research at NRL.
15. Yuanxi Fu received the UIC Department of Chemistry Fellowship

Graduate Students

NAME	PERCENT SUPPORTED
Brian Yulga (UNLV)	1.00
Yuri Skryl (U of Latvia)	1.00
Joe Hooper (Tulane)	1.00
K. McLaughlin	0.00
Ognjen Grubor Urosevic	0.05
Aaron Lozano	0.50
Yee Kan Koh (UIUC)	0.00
Mark Conroy (USF)	1.00
Jeffrey Carter (UIUC)	0.00
Yuanxi Fu (UIC)	0.50
Yoonsoo Pang (UIUC)	0.00
Ying Fang (UIUC)	0.00
Martin Galley (UNLV)	1.00
Rusty Connor (UIUC)	0.25
Aaron Landerville (USF)	0.50
Mikalai Budzevich (USF)	0.50
Edward Romano (UNLV)	0.05
FTE Equivalent:	7.35
Total Number:	17

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Dr. Hubertus Giefers (UNLV)	0.00
Dr. Cedric Gobin (UNLV)	0.08
Dr. Anna Kimmel (UNLV)	0.75
Dr. Baj-Hyun Seong	0.00
Dr. Shinsuke Shigeto	0.00
Dr. Zhaohui Wang	0.00
Dr. Prahuddha Mukerjee	0.75
Dr. Selezion Hambir (UIUC)	0.25
Dr. Alexei Lagutchev (UIUC)	0.01
Dr. Zhaohui Wang (UIUC)	
Dr. Nak-Hyun Seong	0.00
Dr. Hiroki Fujiwara	0.00
Dr. Onice Sharia	1.00
Dr. L. Wang	1.00
Dr. Ying Chang (UNLV)	0.33
Dr. Sergey Tkachev (UNLV)	0.10
Dr. Nikolai Zarkevich (UMd)	1.00
FTE Equivalent:	5.27
Total Number:	17

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Ivan Oleynik (USF)	0.02	No
Malcolm Nicol (UNLV)	0.03	No
Prof. Sergey Rashkeev		No
Michael Pravica (UNLV)	0.03	No
Dana Dlott (UIUC)	0.02	No
Maija Kukla (U Maryland)	0.00	No
Prof. Tao Pang (UNLV)	0.00	No
Prof. Oliver Tschauner (UNLV)		No
Prof. Boris Kiefer	0.00	No
Prof. Krystina Lapinka-Kalita	0.00	No
Prof. Sergey Rashkeev (Vanderbilt)	0.00	No
Prof. Alexandar Roytburd (U Maryland)	0.00	No
Prof. Chulsung Bae (UNLV)	0.00	No
Prof. Eunja Kim (UNLV)	0.10	No
FTE Equivalent:	0.20	
Total Number:	14	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Ms. Anna Belak	1.00
Mr. Sean Bajar (UNLV)	0.05
John Paul Badasci (UNLV)	0.05
Mr. Ben Sundell (U. Tennessee)	0.05
Ms. Jeralie Orwig (UNLV)	
Mr. Edward Romano (UNLV)	0.20
Mr. Zachary Quine (UNLV)	0.20
Francisco Sermeno (UNLV)	0.05
Martin Galley (NSF REU SUNY Cortla	0.05
Yu Zhen Feng (UNLV)	0.05
Yu Liu (Green Valley HS and now UNI	0.00
Mr. Harrison Ruiz (UNLV)	0.05
Ms. Jennifer Wojno (UNLV)	0.05
Mr. Michael Haire	0.50
Mr. Jeremy Segafredo (UNLV)	0.10
FTE Equivalent:	2.40
Total Number:	15

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	5.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	4.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	4.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	3.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	1.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	3.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Brian Yulga (UNLV)
Edward Romano (UNLV)
Ognjen Grubor-Urosevic (UNLV)
Aaron White (UIC)
Total Number:

4

Names of personnel receiving PHDs

<u>NAME</u>
Yoonsoo Pang (UIUC)
Michael Conroy (USF)
Total Number:

3

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	
Natalia Zimbovskaya (U Maryland)	0.10	No
Neelanjan Bhattacharya (UNLV)	0.25	No
Dr. Zhenxian Liu (NSLS, Carnegie Ge	0.00	No
Alexandar L. Shluger	0.00	No
Peter V. Sushko	0.00	No
Frank Zerili	0.00	No
David S. Moore	0.00	No
Daniel Hooks	0.00	No
Dr. Sergey V. Zybin	0.00	No
Dr. Carter T. White	0.00	No
Professor Igor Plaksin	0.00	No
Prof. Boris Kiefer (NMSU)	0.00	No
Dr. Michael Glazov	0.10	No
FTE Equivalent:	0.45	
Total Number:	13	

Sub Contractors (DD882)

1 a. University of Maryland - College Park

1 b. Research Admin. & Advancement

University of Maryland

College Park MD 207425141

Sub Contractor Numbers (c): 05-655K-0000

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): To conduct fundamental theoretical studies of insensitive energetic materials under extreme conditions

Sub Contract Award Date (f-1): 11/1/2005 12:00:00AM

Sub Contract Est Completion Date(f-2): 12/31/2007 12:00:00AM

1 a. University of Maryland - College Park

1 b. Office of Research Administration

and Advancement

College Park MD 207425141

Sub Contractor Numbers (c): 05-655K-0000

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): To conduct fundamental theoretical studies of insensitive energetic materials under extreme conditions

Sub Contract Award Date (f-1): 11/1/2005 12:00:00AM

Sub Contract Est Completion Date(f-2): 12/31/2007 12:00:00AM

1 a. University of South Florida at Tampa

1 b. 4202 East Fowler Ave.

Tampa FL 33620

Sub Contractor Numbers (c): 05-655K-0000

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): To conduct fundamental, theoretically-based studies of insensitive energetic materials under extreme conditions

Sub Contract Award Date (f-1): 1/1/2005 12:00:00AM

Sub Contract Est Completion Date(f-2): 9/30/2010 12:00:00AM

1 a. University of South Florida at Tampa

1 b. Division of Sponsored Research

4202 East Fowler Avenue, FAO126

Tampa FL 336207900

Sub Contractor Numbers (c): 05-655K-0000

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): To conduct fundamental, theoretically-based studies of insensitive energetic materials under extreme conditions

Sub Contract Award Date (f-1): 1/1/2005 12:00:00AM

Sub Contract Est Completion Date(f-2): 9/30/2010 12:00:00AM

1 a. Vanderbilt University

1 b. PMB # 407749

2301 Vanderbilt Place

Nashville TN 372407749

Sub Contractor Numbers (c): 05-655K-0000

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): To conduct fundamental and theoretically-based studies of insensitive energetic materials under ext

Sub Contract Award Date (f-1): 1/1/2005 12:00:00AM

Sub Contract Est Completion Date(f-2): 12/31/2007 12:00:00AM

1 a. Vanderbilt University

1 b. Division of Sponsored Research

512 Kirkland Hall

Nashville TN 37240

Sub Contractor Numbers (c): 05-655K-0000

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): To conduct fundamental and theoretically-based studies of insensitive energetic materials under ext

Sub Contract Award Date (f-1): 1/1/2005 12:00:00AM

Sub Contract Est Completion Date(f-2): 12/31/2007 12:00:00AM

1 a. University of Illinois - Urbana - Champaign

1 b. Office of Sponsored Programs

1901 S. First Street

Champaign IL 61820

Sub Contractor Numbers (c): 08-655K-A-00

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): Conduct fundamental experimental studies of insensitive energetic materials under extreme and dyn

Sub Contract Award Date (f-1): 4/8/2008 12:00:00AM

Sub Contract Est Completion Date(f-2): 9/30/2010 12:00:00AM

1 a. University of Illinois - Urbana - Champaign

1 b. Grants & Contracts Office

Office of Business & Financial Services

Champaign IL 618207406

Sub Contractor Numbers (c): 08-655K-A-00

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): Conduct fundamental experimental studies of insensitive energetic materials under extreme and dyn

Sub Contract Award Date (f-1): 4/8/2008 12:00:00AM

Sub Contract Est Completion Date(f-2): 9/30/2010 12:00:00AM

Inventions (DD882)

Scientific Progress

MURI Final Report

Scientific Progress and Accomplishments

This Multidisciplinary University Research Initiative project, administered by the UNLV High Pressure Science and Engineering Center (HIPSEC), entailed a fundamental aim the determination of fundamental properties of solids with and without defects under extreme conditions (high static pressures, elevated temperatures, and high ionizing radiation flux) to understand how defects and phase changes contribute to initiating and affect the rates of decomposition reactions. We have determined equations of state and the related physical properties for a series of crystals via experimental and theoretical/computational methods.

We have collected optical, infrared, and Raman spectra and x-ray diffraction patterns of energetic materials under extreme conditions. Where possible, these results have been compared with theoretical calculations, qualitatively and quantitatively gaining much insight into the behavior of energetic materials under extreme conditions (such as might be experienced during the initiation and propagation of a shock wave).

We have introduced students at all levels to relevant scientific and engineering problems as a critical component of our efforts and have brought them to our national experimental facilities such as the APS and the NSLS. We have observed and continue to anticipate that exposure to these problems and facilities during student years will motivate some excellent students to consider careers with DoD, their laboratories, other government laboratories and defense-related businesses. Our program has been constructed on our existing interdisciplinary education program at UNLV and elsewhere. Extensive collaborations with industrial, government, and academic laboratories that share similar scientific interests and have complementary skills have occurred. We approached our tasks by involving full-time postdoctoral and part-time graduate and undergraduate students and even high school students throughout the year. Each summer, we involved undergraduate students in UNLV's Research Experience for Undergraduates Programs.

The students who worked on this project also participated in common activities related to developing research careers with other REU students supported by DOE, NSF EPSCoR and REU programs. Whenever possible, students and postdoctoral scholars were offered research opportunities at government labs to gain unique hands-on/minds-on experience from lead energetic materials scientists. We supported these short-term visits from MURI funds.

During the nearly 66 months covered by this report, we organized our activities, hired postdoctoral scholars for the theory activity, expanded upon experiments initiated under aegis of HIPSEC's DOE-funded activities, and began new experimental programs. MURI participants at UNLV also received a modest companion award from the Soldier FERST Cooperative Agreement with the Army Research Laboratory to study vibrational spectra of defect-free energetic materials including many of direct interest to this project.

MURI participants generated 50 peer-reviewed publications during the award period with two additional submitted manuscripts currently under review. Members of the team also made 69 presentations at national and international meetings and at universities.

Two doctoral degrees were awarded to students who performed MURI-funded research and four masters degrees were awarded similarly for work that was fully or partially-funded by the MURI grant.

In what follows, we present a brief summary of the highlights of this DOD-supported work. There were three primary thrusts to the effort: static experimental studies of insensitive energetic under extreme conditions, dynamic experimental studies of insensitive energetic under extreme conditions, and theoretical modeling of insensitive energetic materials under extreme conditions.

Summary of Static Experimental Efforts (Pravica, Nicol Tschauner):

Over the course of this MURI award, the Pravica group has made significant inroads into better-understanding the following insensitive explosives under extreme conditions: PETN, TATB, HMX, HNFx, and most recently FOX 7. We have also examined other energetic and reactive materials such as 1,3,5,7 cyclooctatetraene (COT) and potassium chlorate (KClO₃) and ringed hydrocarbons such as cyclopentane as a consequence of ideas developed during the course of this award.

Fundamental research has been performed on these DOD-relevant materials using infrared and Raman spectroscopies, x-ray diffraction (both monochromatic angular-dispersive and energy-dispersive white beam) using the U2A beamline at the National Synchrotron Light Source (NSLS) and the High Pressure Collaborative Access Team's (HP-CAT's) facilities at Sector 16 of the Advanced Photon Source where UNLV has a 25% ownership stake. As a consequence of our studies, novel behavior has been observed on the studied materials under extreme conditions and novel effects have been predicted and/or observed. We briefly list the highlights of our studies with each of the materials here:

Studies of TATB:

Triaminotrinitrobenzene is a highly insensitive high explosive (HE) that can be safely machined and is used in situations where insensitivity to accidental detonation is required (such as in nuclear weapons). From a physics perspective, the molecule is highly symmetric and is constructed from an aromatic benzene ring. We have observed that infrared (IR) spectroscopy can have significant advantages over Raman spectroscopy as it does not damage appear to damage our yellow samples which rapidly decomposed in the presence of 514.5nm laser beam. As IR measurements are complementary to Raman spectroscopy, they augment a more complete spectral picture of these important materials. Mid-IR and far-IR high pressure studies of TATB were conducted at the U2A infrared beamline at the NSLS at ambient temperature. These were the first IR studies [check] ever reported at high pressure.

In the case of TATB, we found no compelling evidence for any phase transition up to 30 GPa (though a possible splitting of

spectral lines appeared to begin emerging at 30 GPa). We also found a negative frequency shift of the N-H symmetric and anti-symmetric vibrational lines with pressure suggesting that as the applied pressure is increased, hydrogen bonding strengthens which promotes delocalization of electrons away from the N-H and (possibly) N-O bonds weakening them. All changes were found to be reversible with pressure.

Studies of HMX:

HMX (also known as High Melting eXplosive or Her Majesty's eXplosive) is another ringed insensitive explosive that we examined. Mid- and Far- IR Studies of HMX to 30 GPa have found evidence for three possible phase transitions near 5, 12, and 25 GPa. The transitions near 12 and 25 GPa have been observed using other methods (not IR) but the possible transition near 5 GPa has never before been reported and it will be very interesting to see if there will be any confirmation of this possible phase transition in future studies. We have, at the moment, preliminary and unpublished evidence for this phase in recent EDXRD studies using a Paris-Edinburgh cell at 16 BM-B beamline of HP-CAT. Part of our desire to perform far-IR studies of HMX arose from a request by Prof. Bill Goddard from Caltech at the final MURI review last May, 2010 in an attempt to develop some last minute synergy between the MURI focus groups. Our studies represent the first-reported high pressure studies of HMX in the far-IR range and high frequency mid-IR range (2700-3200 cm⁻¹) and more than quadrupled the prior-investigated pressure range in the lower mid-IR region.

Studies of PETN:

We have examined pentaerythritol tetranitrate as a function of high pressure and variable temperature using IR (NSLS) and Raman (UNLV) spectroscopic and x-ray diffraction (methods. Evidence was observed for a phase transition near 5 GPa under nonhydrostatic conditions which had been previously predicted by Gupta and Dreger. Subsequent high resolution x-ray diffraction studies (Pravica, Tschauner) at the X7A beamline at the NSLS indicate that the transition is ferroelastic in nature. We also performed preliminary studies of PETN under high pressure and high temperature and intend to continue these measurements soon

Studies of RDX (Tschauner):

High resolution x-ray diffraction was employed to examine conformational disorder in HMX-containing α -RDX as function of pressure based on high resolution micro-powder diffraction. The sensitivity of α -RDX depends strongly on its HMX content HMX either as inclusion or as a molecule residing on RDX crystal lattice sites strain the host crystal lattice. In a molecular crystal such as α -RDX, this internal lattice strain may induce local changes in molecule conformation towards more sensitive conformers.

A change in equatorial to axial configuration of two of the nitro-groups matches a recently proposed model for γ -RDX. However, our data are not consistent with complete ordering in this configuration. We see oxygen positional disorder, and we clearly see a structural change from orthorhombic to monoclinic.

Studies of HNFx (Pravica, Nicol, and Kim Groups):

At the request of Dr. Robert Chapman at the Naval Air Weapons center, China Lake, we conducted high pressure studies of HNFx (invented by him) to determine whether or not a predicted higher-density polymorph exists at high pressure. No evidence was found for any phase transition within the 0-30 GPa pressure range in x-ray diffraction, synchrotron IR, and Raman studies. A preliminary equation of state (EOS) was determined. These studies were the first high pressure studies of this novel HE.

Studies of Ringed Hydrocarbons (Pravica and Kim Group):

As some of the HEs that we studied (namely TATB and HMX) have ringed hydrocarbon skeletons, we undertook examinations of various ringed hydrocarbons to ascertain their stability under extreme conditions. Also, HEs are often mixed with fuel oils as well so we sought to separately investigate these materials which can also be considered energetic materials. From our investigations, we have also argued that the interaction between the aromatic rings and the nitro/amine groups plays a vital role in determining the instability of the HE and thus detonation sensitivity. As a consequence of our investigations, we sought to investigate the effects of pressure on the aromatic character of ringed hydrocarbons. We have predicted and observed unusual behavior in 1,3,5,7 cyclooctatetraene which was developed by the Nazis as a possible propellant/HE. The idea was to "flatten" the molecule with pressure either mechanically by driving conformational changes from the tub shape or via electronic transfer as COT⁻ and COT²⁻ are aromatic radicals. From a quantum-mechanical point of view, flattening the molecule would force symmetry driving into an aromatic state. Aromatic molecules tend to be very chemically stable. Thus, our reasoning led us to believe that by driving an aromatic molecule out of aromaticity, it might be very reactive. This is the future direction that the Pravica group research will follow (molecular changes in aromaticity as a function of pressure) - funding permitted.

We performed the first high pressure studies of this molecule and found evidence for at least two phase transitions of the molecule within the 20 GPa pressure range as well as irreversible reactions above 17 GPa. Further study, particularly with high pressure NMR would be very helpful. In that spirit, Prof. Pravica has begun preparations to perform high pressure NMR at UNLV which was the subject of his thesis work at Harvard.

We also studied cyclopentane to above 20 GPa, nearly quadrupling the prior-investigated pressure range of the molecule. Evidence from our studies suggest that phase III and phase IV are really similar where phase IV is a "frozen-in" conformation of phase III.

Studies of FOX7 (Pravica Group):

FOX 7 (also known as DADNE- DiAmino DiNitro Ethylene) is a recently-developed HE that shows much promise as a high energy insensitive explosive. Few high pressure studies and high temperature studies had been performed on this HE prior to our investigations. As FOX 7 has many similarities to TATB (both compounds are yellow, possess significant graphitic-like interlayer bonding, strong intra-layer hydrogen bonding, and both have alternating nitro and amine groups e.g.) we were interested in studying this material under extreme conditions. There have been significant theoretical efforts from Prof. Kukla from our MURI team thus, we sought to connect our experimental efforts with the Kukla team's work. Finally, FOX 7 is more sensitive than TATB. Understanding why is of paramount importance. We believe that part of the reason for this phenomenon pertains to the fact that TATB is aromatic in its' carbon skeleton whereas DADNE only has a C=C skeleton. Thus, from the standpoint of aromatic stability, one might naively guess that TATB is less sensitive to detonation than FOX 7. Future studies should further examine this question.

As FOX 7 is extremely difficult to obtain outside of Sweden where it was developed, we synthesized the HE "in house" in the laboratory of Prof. Chulsung Bae in the UNLV chemistry department.

We conducted high pressure and high temperature studies using the Paris-Edinburgh cell to employ larger samples volumes in an attempt to examine behavior approaching (but not reaching) the detonation threshold determining the phase line between the α phase and probably the γ phase at high pressures (below 3 GPa) and high temperatures (in the 1000 K range). Our studies represented the first-reported investigation of FOX 7 at high pressure AND high temperature.

Studies of Melamine (Pravica Group):

Melamine is a ringed aromatic, highly-symmetric, molecule that appears very similar to TATB except that it is missing the $-\text{NO}_2$ groups and has three alternating nitrogen atoms instead of carbon in the 6-member benzene skeletal ring. Yet, unlike TATB, melamine is considered to be very stable and is even used as a fire retardant and foundation of dishware. It is also believed to be a precursor to superhard C_3N_4 synthesis. We performed a variety of experiments (IR, Raman, and x-ray diffraction) with pressure many of which have more than doubled the prior-investigated pressure range of the material. We are currently composing a manuscript to report our IR results up to 30 GPa of pressure. We also performed the first in-situ measurement of melamine at high pressure and high temperature verifying the presence of molecular reaction above 1000 K and near 5 GPa of pressure. The results have been reported in a manuscript submitted to Diamond and Related Materials (DIAMOND 2011 conference proceedings) last September 2010 and are currently under review. This work on melamine formed the basis of Mr. Martin Galley's masters thesis work at UNLV and he is hoping to defend his thesis this summer (2011).

Summary of Dynamic Experimental Studies (Pravica, Nicol, and Dlott Groups):

X-ray induced decomposition of PETN, HMX, and TATB (Pravica Group):

During an attempt to measure x-ray Raman spectra of PETN and TATB at 16 ID-D of HP-CAT at the APS, rapid decomposition was noted of the HEs with time due to x-rays. We resolved to measure this decomposition rate as an aid for future investigators and to calibrate our damage. We used white beam radiation available at the 16 BM-B and 16 BM-D beamlines to examine HE decomposition rates as a function of pressure. by examining the strength of the diffracted signal from PETN and TATB powder in a diamond cell. We observed no change in the decomposition rate with pressure in PETN but observed a slowing of decomposition rate with increase in pressure suggesting that the sign of the activated reaction complex volume is positive. This is in itself a very challenging measurement to do otherwise. In the words of Nobel Laureate, Ahmed Zewail, our "paper is considered as a significant contribution to the field."

Subsequent work on the white-beam x-ray induced decomposition rate for HMX using a Paris-Edinburgh cell has qualitatively demonstrated a similar slowing of the decomposition rate with pressure as with TATB. This may be due in part to the fact that both HMX and TATB are ringed HEs whereas PETN (which did not show similar decomposition rate behavior) is not. Future work will endeavor to examine other ringed HEs such as RDX and non-ringed HEs such as FOX 7 to further our hypothesis.

Anisotropic Decomposition of PETN (Pravica Group):

Over the course of Prof. Pravica's studies of x-ray- induced decomposition of HEs, the idea of anisotropic decomposition of organic materials based on the interaction of the polarized x-ray beam with various oriented bonds bore fruit. After all, it is well known that single-crystal PETN exhibits strong anisotropic behavior in detonation sensitivity. Why not in decomposition? Using high quality and relatively large (but below the 10 mg detonation limit) single crystals of PETN, we subjected the crystals to white x-ray beams and recorded the x-ray diffraction signal using an x-ray CCD or image plate recorder. By monitoring the intensity of the manifold of x-ray diffraction spots as a function of time within the same crystalline orientation, dramatic differences of the decomposition rate were observed in different spots. It is our hope that at some point in the future, this novel effect will be used to determine the weakest bonds in crystals as they would likely break most rapidly and thus perhaps aid in better-determining a mechanism for molecular breakdown of some HEs. It should also be mentioned that efforts were made to examine TATB using this technique. Due to the poor crystal quality (which is largely due to the strong intra-layer hydrogen bonding) of TATB, it was difficult to find isolated spots to compare decomposition rates. Nevertheless, examining damage tracks in crystals of TATB demonstrated the utility of using the highly focused ($<30\text{ }\mu\text{m}$) x-ray beam to engender damage

without damaging the rest of the crystal. Thus, x-ray induced damage, far from being a nuisance in measurements, can be used to create highly localized molecular damage for further study of damage mechanisms.

As FOX 7 crystals appear to be of much higher quality, we would like to attempt future anisotropic measurements on this HE.

Nanoscale Structure and Dynamic Response. (Dlott Group):

For the performance period of 1 Sep 2007 to 8 Apr 2008 this project was funded as a Caltech subcontract. On 8 Apr 2008, the project was moved to UNLV. The goal of this work entailed understanding initiation processes of energetic materials (EM) on fundamental length and time scales (atoms to microns, femtoseconds to nanoseconds), in order to develop a deeper knowledge of what makes an EM more or less sensitive. The Dlott group subproject accomplished this goal by measurements of EM structures, EM reactivity and EM vibrational energy dynamics by means of:

- Vibrational sum-frequency generation spectroscopy of EM surfaces and interfaces
- Ultrafast infrared spectroscopy combined with laser flash-heating
- Ultrafast Raman or SFG spectroscopies combined with flash-heating or IR vibrational pumping

Surface spectroscopy of HMX and RDX.: The Dlott Group's third generation Sum Frequency Generation (SFG) laser system has been harnessed to study nitro groups on the surfaces of RDX and HMX. We have made great improvements in sensitivity. An important new technique has been developed using time delayed asymmetric picosecond laser pulses to eliminate the nonresonant background of SFG spectra. This nonresonant background greatly hinders one's ability to interpret SFG spectra. We have completed a detailed study of vibrational energy transfer in nitromethane and deuterated nitromethane using an ultrafast Raman method.

Vibrational energy flow through EM simulants.: An exciting new method to study vibrational energy in HEs has been developed. A monolayer of molecules is bound to a surface, typically a gold surface where the attachment is made by thiolate linkages. The gold is temperature jumped to a high temperature, typically 1100 K, while the molecules are monitored by SFG (thermal shock). With this technique we can vary the molecular structure atom by atom at study how the vibrational energy flow is affected. We first studied a model system of alkane thiol molecules to show we could measure the speed of vibrational energy flow along a molecular chain. Then we studied substituted benzene molecules of the form (hot gold surface)-S-(phenyl)-CH₃. We were able to measure the rate at which vibrational energy flowed from the surface into the phenyl ring and also from phenyl into methyl. We are currently synthesizing HE-stimulant molecules, which are benzene thiolates that can bind to the Au surface but have nitro groups at specific locations so that we can probe energy flow through nitro-aromatic groups.

Development of surface-enhanced Raman techniques to study vibrational energy in HEs. The SFG detection technique is a kind of molecular thermometer. It is sensitive to the disorder created in the molecules as they heat up. This provides an overall measurement of the level of vibrational excitation, but it is not specific. SFG is a powerful nonlinear coherent method that makes good signals even from molecular monolayers. The way to measure heat flow by measuring the amount of energy in each molecular level is to use Raman spectroscopy, as in our nitromethane studies. But Raman spectroscopy is too weak to study monolayers unless a photonic substrate enhances the signal. This is "surface-enhanced Raman scattering" or SERS. Preliminary measurements have been performed of aromatic molecules on photonic substrates in order to find the conditions needed to study these molecules with Raman scattering. Nobody has yet been able to use femtosecond pulses to study molecules on such substrates because of the ease of damaging the molecules. We measured this laser damage very carefully and in the process we have answered an important question about how SERS works. This SERS paper has just been published in Science. Now we have a roadmap for making these measurements on HE simulants and we are fabricating novel photonic substrates and setting up the laser to do it.

Among other more recent accomplishments made by the Dlott group:

- A method of determining the structure and orientation of nitro groups on the surfaces of HEs was developed by combining measurements of the polarized vibrational spectrum of surface nitro groups as a function of crystal orientation (rotation about an axis) with calculations of the molecular hyperpolarizability.
- A method to study "heat shock," which is the flow of a large quantity of energy input at one point of a molecule and probed at another point, was developed and the method was used to study energetic molecule simulants in a self-assembled monolayer.
- A method to measure the vibrational spectrum at high pressures of monolayers of molecules such as RDX and HMX that comprise important energetic materials, or energetic material simulant molecules was also developed.
- Significant improvements in the sensitivity of probing vibrational transitions of HE simulant molecule monolayers under dynamic shock compression by using a method that suppresses the nonresonant background that is generated by the metal surface, coupling liquid and shock confinement window in a shock target array.

Summary of Theoretical Studies of High Explosives (Kuklja and Oleynik Groups):

1. Equations of State from ab initio Calculations: (Kuklja and Oleynik Groups):

FOX 7 and HMX EOS (Kuklja Group):

Significant efforts have been made to determine the equations of state of various insensitive HEs such as FOX 7 and HMX. Predicting the behavior of these materials under the extreme conditions that can be endured when sustaining a shockwave is of

great importance. As organic molecules tend to be very flexible and have many complex intra- and inter-molecular interactions, prediction of the equation of state (EOS) at any temperature can be extremely challenging. On top of this, measuring the EOS of HEs has also been complicated by the difficulties associated with performing x-ray experiments with nanoliter samples and the generally low symmetry (and thus high number of diffraction lines which often overlap) of their unit cell structures.

Nevertheless, the Kuklja group has made significant inroads toward prediction of the EOS of FOX 7 and HMX using a wide variety of calculational tools such as Density Functional Theory (DFT) CRYSTAL98 computer program, using the Hartree-Fock method and a linear combination of atomic orbitals basis set (6-21G in Pople's notation). Scaling factors were applied to the outer valence orbitals, reducing their range, to adapt what would normally be a basis set optimized for isolated clusters of atoms for use in a periodic structure computation. Optimizations of the atomic coordinates and lattice parameters were done separately and iteratively. The atomic coordinates were first optimized using Zicovich-Wilson's LoptCG script, which calls CRYSTAL98 to calculate the energy for each configuration. The lattice parameters then were optimized under a fixed volume constraint for a set of volumes presenting a number of hydrostatic compressions using a locally written program based on the downhill simplex method of Nelder and Mead. This was repeated until satisfactory convergence was achieved. No correction for basis set superposition error was made and the close agreement with experiment may be fortuitous due to cancellation of basis set errors with lack of treatment of van der Waals forces with the Hartree-Fock method. Calculations with the Perdew-Wang generalized gradient approximation (GGA) density functional theory method (DFT), corrected for basis set superposition error using the counterpoise method of Boys and Bernardi, while reproducing the equilibrium unit cell volume reasonably well, severely underestimated the bulk modulus under compression. For this reason, we choose here to rely on the results of the Hartree-Fock calculation for the mechanical compression curve.

The Kuklja group also performed calculations to determine the vibrational contribution of the EOS in FOX 7 to better ascertain the temperature-dependence of the EOS. Ab initio calculations were performed to extract the complete equation of state for an organic molecular crystal over a pressure range from 0 to 4 GPa and a temperature range of 0 to 400 K. The 0 K isotherm was obtained by numerically solving the many body Schrödinger equation using the Hartree-Fock method with a computational scheme utilizing a basis set consisting of linear combinations of atomic orbitals as implemented in the computer program CRYSTAL98. A complete description of the 0 K isotherm calculations was reported in earlier publications. The $T > 0$ vibrational contributions to the Helmholtz free energy were obtained in the quasiharmonic approximation from solutions to the Schrödinger equation using density functional theory methods as implemented in the computer program ABINIT, a plane wave pseudopotential code developed by Gonze, et al.

Finally, A complete equation of state for the molecular crystal 1,1-diamino-2,2-dinitroethylene was calculated from first principles for temperatures between 0 and 400 K, and for specific volumes from 61 to 83 cm³/mole, corresponding to relative volumes from 0.78 to 1.06. The calculated 300 K isotherm agrees very well with the experimentally measured pressure-volume relation. The volumetric thermal expansion coefficient is calculated to be 140 ppm/K at 300 K and atmospheric pressure and varies considerably with specific volume as well as temperature. The Grüneisen parameter varies significantly with temperature but its variation with specific volume is small. The calculated specific heat (160 J/mol/K at 300 K and atmospheric pressure) has only a very small dependence on specific volume.

Mechanical compressibility of nitromethane at low temperatures (Kuklja group):

The mechanical compressibility of solid nitromethane has been examined at high pressures by using Hartree-Fock (HF) and DFT with atom-centered all-electron basis sets. The HF calculations with a 6-21G basis set, uncorrected for basis set superposition error, gave the best agreement with experimental compression studies. These results may be due to the cancellation of basis set superposition error with the lack of dispersion force contribution to the total energy. The 6-21 G HF approach produces results most agreeable with experiment because of cancellation of errors. The trend is observed for several energetic materials and gives hope that this method can be widely used for predicting cold compression of HE materials.

First-principles equations of state (EOS) of energetic materials (Oleynik group): The USF team performed systematic theoretical investigations of several important energetic materials (EMs) including PETN, HMX, and RDX at high compression using first-principles density functional theory (DFT). Accurate equations of state (EOS) are of particular interest because they establish fundamental relationships among thermodynamic variables and provide necessary input for describing materials at the mesoscopic and continuum levels. Ultimately, these EOS are governed by interactions at the atomic scale, which provides an excellent opportunity for atomic-scale simulations techniques to link the microscopic and macroscopic properties of materials. In addition to isotropic EOS, i.e. relationships between pressure and volume, we investigate the anisotropic EOS, i.e. dependence of stresses on uniaxial compressions along several crystallographic directions. Because of the dominant role of shock-induced phenomena during initiation and propagation, the anisotropic EOS is of highest interest of experimental EM community. Within this MURI project, the Oleynik group made an important breakthrough by developing theoretical and modeling techniques for investigating anisotropic EOS. By applying these simulation tools, information was obtained that is very difficult to obtain by experimental means. In FY08, the USF team investigated the anisotropic EOS (AEOS) of HMX in addition to completing AEOS for PETN. The AEOS was obtained for uniaxial compressions in the directions normal to the {100}, {010}, {001}, {110}, {101}, {011}, and {111} planes of β -HMX have been performed to investigate the anisotropic equation of state (EOS).

In subsequent work, the USF team worked on the development of accurate equations of state for energetic materials based on van-der-Waals corrected density functional theory (DFT). Although DFT has been applied to study energetic materials, its accuracy suffers from the poor description of these interactions. For example, in our previous work, first-principles calculations

of Ems using the Perdew-Burke-Ernzerhof (PBE) functional yielded approximately 10% error in the unit-cell volumes at zero pressure, and the isothermal equations of state (EOS) consistently showed greater volume at a given pressure than experiment. Further, the unit cells of these systems are rather large, containing approximately 50 to 200 atoms, which makes DFT calculations rather costly. The additional cost associated with implementing an exchange correlation functional to account for nonlocal vdW interactions in DFT calculations of EMs is prohibitive. Instead, an empirical approach has the potential to increase the accuracy of first principles calculations involving these systems at a relatively negligible additional cost. An empirical vdW interaction was added to DFT to improve the predictive capabilities of first-principles calculations of energetic molecular crystals. The vdW correction is in the form of pair potentials where the resulting energy, forces, and stress are simply added to those of the DFT calculations. The developed simulation tools were applied to obtain highly-accurate zero-pressure structure. Hydrostatic-compression simulations were also performed on energetic molecular crystals of FOX 7, HMX, RDX, PETN, nitromethane, and TATB, and compared with both USF- previous calculated results and experiment demonstrating a reduction in error between theory and experiment using this novel method. These and other tools were applied to predict EOS of newly synthesized EM NEST-1 ahead of experiment and the vdW-DFT-T is being applied to obtain important temperature-dependent physical properties of EMs not available from experiment at the present time.

2. Theoretical Computations Associated with Chemistry Under Extreme Conditions (Kuklja group):

The Kuklja group performed a number of computations aimed at better understanding chemistry under extreme conditions – primarily associated with shock wave initiation and propagation within a HE. We list major highlights of these efforts below.

A Continuum Model Study of Shock-induced Polarization – Numerical Simulations of Shock-induced Polarization in Binary Electrolytes: The shock-induced polarization in aqueous KF was computed by coupling a complete system of diffusion equations for charge carriers with the Poisson equation and solving them simultaneously. The results demonstrate that the space charge induced by the diffusive separation of potassium and fluoride ions in the shock wave affects polarization currents and depends on the KF concentration. This is consistent with the experimentally observed inversion of polarization current. This simulation suggests that, for a critical concentration of XKF, currents are caused by polarization of water and that concentration changes affect only physical properties of the solution, most likely the viscosity, which also alters the polarization signal. Presumably, both the inertial diffusion of charge carriers and the polarization of water could cause of the inversion of polarization signal. As a consequence of these efforts, a novel and consistent method for studying polarization of electrolytes based on diffusive separation of ions induced by the shock wave has been proposed. An explicit simulation of the polarization process is performed by means of a numerical solution of the electro-diffusion equation system coupled with the Poisson equation. Shock wave loading was assumed to be a source for the stress field that triggers diffusive separation of ions in the solution. The results obtained prove that the ionic mechanisms of polarization take place only in strong electrolytes and may be responsible for the inversion of the polarization signal observed experimentally.

Polarization in Distilled Water: A detailed analysis of experimental work by Eichelberger and Hauver (1961) was performed based on an orientation polarization mechanism of water, which is analytically described here in great detail. First, the notion of coexistence of stress and inertial forces is introduced to explain a shock-induced alignment of water molecules in such a way that hydrogen atoms are always moving in front of oxygen atoms along with the shock wave front progressing across the material. Next, the structure of the shock wave front is considered and specifically the obtained width of the front is discussed. Furthermore, the induced by shock polarization is calculated based on the stress and inertial contributions into the total and specific parameters of the shock wave in water. This allows definition of the polarization charge and description of the formation of the double charged layer within the shock front or distributed over the entire sample depending on the charge relaxation time. This in turn is determined by the dynamics of water viscosity behind the front. The polarization characteristics of water, electric field, potential and bias current, were calculated from the polarization charge density, and agree well with experimental data of Eichelberger and Hauver. Finally, it was concluded that the re-orientation of water molecules is a dominating mechanism of shockinduced polarization.

A Quantum-chemical Study of Shear-induced Chemistry: The electronic structure and decomposition mechanisms in crystalline FOX-7 were investigated. A simulation of a reversed-orientation-molecule and shear strain defects was undertaken, which should be very representative of elements of such common defects in molecular crystals such as dislocations, stacking faults, and grain boundaries. In spite of the fact that in the FOX-7 crystal the electronic structure is mostly defined by intramolecular interactions, intermolecular interactions play a crucial role in the decomposition process. The perfect crystal is relatively stable, the decomposition barrier associated with C-NO₂ bond breaking being about 92 kcal/mol (4 eV), much higher than the experimentally measured one. The presence of reversed-orientation-molecule defects produces broken C-NO₂ bonds at 59 kcal/mol in excellent agreement with experiment. The shear strain defect may reduce the decomposition barrier even further. All of these defects reduce the band gap by changing the hybridization between the N-p and O-p molecular orbitals thereby introducing new local electronic states.

Formation of a Polydomain Structure and Incoherent Interfaces at Polymorphic Transformations in Energetic Crystals: The theory and phase field modeling of formation of micro- and nano-structure as a result of polymorphic transformations in

energetic materials. This is a necessary step for understanding of mechanisms of detonation because coherent and incoherent interfaces can serve as hot spots for initiating of detonation. A model of the structure and mobility of dislocation interfaces and compared it to the model of mobility of incoherent interfaces through the virtual melting of stressed crystals (Figure 27). The effect of stress on solidification and melting has been studied. It was concluded that the model of dislocation interfaces can be energetically more preferable than the model of virtual melting. Application of these models to polymorphic transformations in HMX crystals has been investigated. The model of domain structure formation due to ferroelastic polymorphic transformations (with possible application to PETN) was proposed.

Density-Functional-Theory Quantum-Chemical Study of Shear-induced Chemical Reactivity in Diamino-dinitroethylene (FOX-7) and Triamino-trinitrobenzene (TATB): Shear-induced decomposition in molecular and crystalline FOX-7 and TATB was investigated via ab initio calculations. The shear strain deformation can significantly reduce the decomposition barrier in FOX-7 but does not affect the decomposition in TATB. This study demonstrated that shear-strain plays a crucial role in dissociation of molecules in organic energetic crystals. A fundamental difference between the crystalline solids TATB and FOX-7 arises when shear-strain is introduced into the lattices. The shear strain deformation can significantly reduce the decomposition barrier in FOX-7 but does not affect the decomposition in TATB. This fact may help to explain why FOX-7 is more sensitive than TATB. This study demonstrates that shear-strain plays a crucial role in dissociation of molecules in organic energetic crystals.

An Effect of Charged and Excited States on the Decomposition of 1,1-Diamino-2,2 dinitroethylene Molecules in the Gas Phase: The electronic structure of individual FOX-7 molecules, its positively and negatively charged states, as well as the lowest excited states were studied by means of DFTG. Two competing initiation mechanisms of FOX-7 decomposition were found: C-NO₂ bond fission and C-NO₂-to-CONO isomerization. Electronic excitation or charging of FOX-7 disfavors CONO formation and, thus, terminates this channel of decomposition. However, charge trapping and/or excitation of CONO-rearranged molecule results in spontaneous splitting of a NO group accompanied by the energy release. Intramolecular hydrogen transfer is found to be a rare event in FOX-7 unless free electrons are available in the vicinity of the molecule, in which case HONO formation is a feasible exothermic reaction with low energy barrier. An important result is that charging and excitation have dramatic effects on the mechanisms of decomposition because they can not only reduce the activation barriers for decomposition reactions, but also change the dominating chemistry from an endothermic to an exothermic type.

Embedded Cluster Model (ECM): A novel Quantum Mechanical /Molecular Mechanical (QM/MM) method has been developed for modeling the structure of and processes in energetic materials. The method is tested on DADNE crystals and applied to simulations of initiation chemistry including a hydrogen transfer and HONO formation as a potential precursor for the thermal decomposition of DADNE and TATB crystals. The method is implemented in the in-house written code GUESS and is expected to be applicable to other energetic materials.

Dissociation Mechanisms in Solid State FOX 7: The earliest stages of the thermally activated decomposition chemistry of DADNE in the condensed phase are modeled by an ECM combined with the Density Functional Theory (DFT). A study of the interplay of C-NO₂ bond fission and nitro-to-nitrite isomerization with the subsequent NO elimination in condensed and gas phases was conducted and compared with available experimental data. It was argued that chemical reactions in solid state explosives are essentially a collective phenomenon of a crystalline field and intermolecular interactions. It was suggested that in the gas phase, DADNE decomposes via two competing isoenergetic mechanisms: C-NO₂ bond scission and nitro-to-nitrite isomer precursor formation. On the contrary, in the solid state, the early chemistry was found to be triggered solely by a slow two-step decomposition process: CONO formation with the consequent NO elimination. The process can be suppressed, however, by a faster C-NO₂ rupture only at higher temperatures or on structural defects. The calculated results imply that the CONO pathway is favored under moderate thermal heating while C-NO₂ bond scission is favored under shock or impact initiation conditions.

Modeling Hydrogen Transfer in DADNE and TATB: Intra- and intermolecular hydrogen transfer was investigated in crystalline DADNE and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) by means of the ECM and DFT. It was found that even though both of these materials have similar amino- and nitro- functional groups as well as layered crystalline structures, there are important differences in the mechanisms of hydrogen transfer. In particular, calculations suggest that proton migration from an amino-group to a nitro-group of the same molecule is a feasible process in TATB but not in DADNE. At the same time, it was found that no intermolecular hydrogen transfer occurs in either molecular crystal. These results imply that the activation of the decomposition reactions proceeds via different paths in these two materials.

Thermal Chemistry Triggered by Stereo-isomer defects in DADNE: An investigation of the structure and properties of crystalline DADNE containing a stereo-isomer molecule (cis- and trans- DADNE) has been performed by means of ab initio DFT and QM/MM ECM simulations. The isomers are considered as a model structural defect, the perturbation of which is localized within the nearest molecules. It was found that the trans-DADNE isomer embedded in an ideal DADNE crystal significantly affects the thermal stability, electronic structure, and chemical and physical properties of the solid DADNE matrix. The resulting conclusions may have implications in understanding the sensitivity to initiation of detonation of energetic materials.

Complexity of Shear-Strain-Induced Chemistry in DADNE: Simulation of shear-induced chemical decomposition reactions of

crystalline DADNE was performed by means of DFT and ultrasoft pseudopotentials. It was shown that the shear-strain deformation plays a crucial role in defining the sensitivities of explosive crystals to initiation and strongly depends on the shape of crystalline layers constituting the material. By focusing on the molecular nature of the shear-strain-induced chemistry, it was found that energetic barriers for DADNE decomposition are affected by shear-strain in different ways. For example, a higher activation barrier of C-NO₂ bond fission decreases because of shear by about 50% while a series of lower activation barriers in the course of the C-NO₂→CONO→CO-NO bond fission increase due to shear deformation. These simulations may help to elucidate ignition mechanisms caused by the mechanical impact or shock and relate these mechanisms to definite types of imperfections such as interfacial deformations, dislocations, stacking faults, or grain boundaries.

PETN and Si-PETN: The project aimed to understanding fundamental differences in the structure, properties, a variety of possible defects, and the correlation of those with sensitivities of regular PETN and recently synthesized Si-PETN. The former is known to be relatively sensitive explosive material, which is well studied at the experimental group at UNLV and, therefore, represents a good model to study theoretically with ab initio and multi-scale techniques. The later material is barely studied since it exhibits a colossal sensitivity to initiation, to the degree that it is able to explode under very minor excitation; its violent nature makes it especially difficult to tackle experimentally.

DADNE. (Kukla, Plaksin): The project aimed to launching a new collaborative effort between the University of Maryland, College Park (Kukla's group) and Coimbra University, Portugal (Plaksin's group), with a primary focus on studying an effect of a radiation emission and heating induced by the shock front, progressing through the material, on sensitivity of DADNE crystals as function of their quality and composition.

HMX phase diagram: The project aims at obtaining a solid state phase diagram for HMX and represents a continuation of the previous work on equation of state being performed in collaboration with F. Zerilli, NSWC-Indian Head. During the past year, we discovered a bug in the ABINIT code, communicated the details of it to the development and support team, and followed up on progress with fixing the error in the latest version of the code. The newest version of ABINIT is free of this bug and is being currently extensively tested. By using this newest version of the code, we are running calculations for equations of state for three crystallographic configurations of HMX (α , β , and δ) to obtain the phase diagram. These calculations are extremely challenging and computer time consuming. We will continue working on this project next year. Should the calculations be successful and converge within some reasonable time yielding the result, it will be possible to implement ab initio equation of state and phase diagrams in the hydrocodes (such as CHEETAH) for better and more accurate modeling.

Oxidation Phase Diagram of Small Aluminum Clusters Based on First-Principles Calculations: A density functional theory study of the structure and properties of Al₁₃ and Al₁₂Ni clusters, oxygen adsorptions on the cluster surfaces, and the completely oxidized clusters was conducted. The relative stability of various phases at various oxygen pressures and temperatures is investigated based on the "atomistic thermodynamics" which was previously employed for studying metal surfaces. The two-dimensional (P,T) oxidation phase diagrams were constructed for these systems. It was observed that alloying the Al cluster with Ni does not improve its resistance to oxidation. The present study provides valuable insight into basic behaviors of small Al clusters in the presence of oxygen and a theoretical basis for exploring practical applications of these clusters. The effect of temperature and oxygen pressure on the stability of various phases is taken into account via oxygen chemical potential. From the obtained oxidation phase diagram, we predict that the oxide phase is preferred in a wide range of practical application conditions, whereas Al clusters with adsorbed O are thermodynamically unstable. The calculated phase diagrams demonstrate that the metal clusters are very easily oxidized. Adding Ni atoms to small Al clusters lacks an advantage of preventing the cluster oxidation. This study provides insight into the oxidation behaviors of Al₁₃ clusters in various environments (O-rich and O-poor).

Effect of Defects on the Initiation Chemistry of HMX: A theoretical study of detonation initiation reactions in crystalline β -HMX was performed by using ab-initio methods. The reaction energies and the activation barriers of two reactions, a HONO-isomer formation followed by HONO elimination and a direct N-NO₂ bond dissociation, (which are considered to be main mechanisms of detonation initiation in HMX) were computed. The same reactions in HMX were analyzed when containing a vacancy or exposed to the shear strain in (001) and (101) directions. Preliminary calculations to build a model of the shear strain deformation have been

performed by constructing an interface between different layers of HMX. A significant change in energy barriers with respect to bulk calculations was noted. This represents an indication that shear strain plays an important role in detonation initiation in HMX which is consistent with previously observed trends in DADNE and TATB and may be used to reveal common features of high explosive initiation behaviors.

Autocatalytic Decomposition at Shear-Strain Interfaces: Atomic scale mechanisms of the initiation of chemical processes in energetic molecular crystals leading to the decomposition and ultimately to an explosive chain reaction, are far from being completely understood. We investigated the onset of the initiation processes in two energetic crystals - diamino-dinitroethylene (DADNE, C₂H₄N₄O₄) and triamino-trinitrobenzene (TATB, C₆H₆N₆O₆). We suggest that an autocatalytic decomposition mechanism is likely to take place in DADNE crystal that is built out of corrugated, dashboard-shaped molecular layers, and the level of the induced shear-strain perturbation between the layers strongly depends upon the presence of interstitial NO₂ groups. Unlike this, in TATB, which consists of flat, graphite-like molecular layers, an interstitial NO₂ group positioned between

two layers produces a local molecular orientation disorder and barely affects the C-NO₂ decomposition barrier. Dissociated NO₂ groups in the interstitial exhibit a series of exothermic reactions. In DADNE, these reactions start at a lower concentration of interstitial NO₂ which may be correlated to the higher sensitivity of this material to the initiation as compared to TATB.

Chemical stability of DADNE and TATB molecules: Ideal crystals containing defects and deformations were comparatively studied from first principles for the first time and their ground state decomposition mechanisms are identified. In DADNE, C-NO₂ break competes with CONO isomerisation as the energetic barrier of C-NO₂ is very sensitive to the presence of imperfections; the dominating reaction switches on shear-strain interfaces from CONO to C-NO₂. In TATB, kinetics and activation of CONO, HONO and C-NO₂ do not depend on induced shear-strain.

A theoretical model of hot spots attributed to shear-strain is developed, however, the effect of the shear-strain deformation on chemical decomposition processes in hot spots is extremely complex and has to be carefully studied further. There are many intricacies to be discovered.

Autocatalytic degradation of shear-strain interfaces is discovered in DADNE and compared to TATB where self-accelerated exothermic chemistry starts at much later time and much higher concentration of primary products.

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