

AD-A137 927

PROPERTIES OF THREE DIMENSIONAL ENERGETIC SOLIDS AND
MOLECULAR CRYSTALS(U) MICHIGAN TECHNOLOGICAL UNIV
HOUGHTON A B KUNZ 01 FEB 84 N00014-81-K-0620

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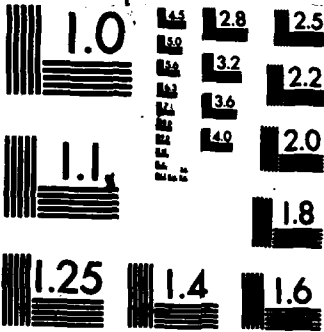
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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER		2. GOVT ACCESSION NO. AD-A137 927	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Properties of Three Dimensional Energetic Solids and Molecular Crystals		5. TYPE OF REPORT & PERIOD COVERED 3rd Annual Technical Report 1 July 1983 - 31 December 1983	
7. AUTHOR(s) Professor A. Barry Kunz University of Illinois at Urbana-Champaign Urbana, IL 61801		6. CONTRACT OR GRANT NUMBER(s) ONR-N-00014-81-K-0620	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Michigan Technological University Houghton, MI 49931		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217		12. REPORT DATE 1 February 1984	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 7	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release: distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Energetic solids, solid fuels, molecular crystals, combustion, excitons, clusters, ab initio theory, nitric oxide, nitric oxide dimer.			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The effect of exciton formation upon combustion of solid fuels is examined by applying ab initio theory to solid and gas phase nitric oxide and its dimer.			

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Technical Report on Grant ONR-N-00014-81-K-0620

Period 1 July 1983 - 31 December 1983

"PROPERTIES OF THREE-DIMENSIONAL ENERGETIC SOLIDS AND MOLECULAR CRYSTALS"

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1. Contract Description.

This project is designed to investigate a wide range of phenomena relating to energetic solids and as appropriate, on other classes of molecular solids. These studies are related to trapping, release and transport of energy in such systems. These studies are all theoretical in nature and are of an ab initio nature. The complexity of some of the systems studied are proving to be a challenge to the state of art, both with respect to available theoretical methods and also computational facilities. In this latter respect the investigators are very fortunate, compared to the average. The Simulation Laboratory at Michigan Technological University provides two VAX 11/750 computers, and soon an FPS 5105 array processor (in a minimal configuration) essentially free to charge to this project. In addition, Professor Kunz has access to the outstanding Center for Computation at the Materials Research Laboratory of the University of Illinois at a nominal cost to defray operating expenses. This facility consists of 3 VAX 11/750 computers, one VAX 11/730 and an FPS 164 Scientific Computer. Unfortunately it is not possible to buy as much time as one needs on this facility. It is proposed to expand this latter facility by adding an FPS 5210 array processor in the near future. This detail is emphasized because we shall later find the needs of this project challenge the finest available facilities.

In the case of solid fuels or explosives the area of relevance to us is the initiation of the combustion process. This may be by means of a strong shock wave or by elevated temperature. In either case our principal aim is to identify the factors which contribute to chemical instability.

The ultimate question of stability of the system and its properties may also be determined by impurities and defects. It is intended to pursue such studies as time permits. Needless to say, one must study all relevant questions in both bulk and surface geometries.

2. Partial List of Unsolved Scientific Questions.

If one excepts the solid rare gases and also now solid Methane there have been little or no studies of three dimensional molecular solids at the ab initio level.

Basically we are ignorant of the simplest spectroscopic details except for a few systems in which the free space molecular spectra and the solid state spectra seem to be in agreement and for which are some free molecular spectroscopic studies. Unfortunately we are not so fortunate when it comes to even simple prototype energetic solids such as NO.

NO exists in free space as the NO molecule and also as a dimer. In the solid state, one believes the solid is composed of dimer NO molecules arranged to have two weakly interacting dimers per unit cell. The solid is believed to be diamagnetic whereas the simple NO molecule is paramagnetic. It might be stated with little fear of gross exaggeration that this is the last known piece of information relating to the fundamental properties of the solid or the NO dimer. The dimer probably exists in a ONNO cis form. However, it seems as if the ONNO trans form is only at a slightly higher energy (a few K-cal/mole). The most recent calculations published on the dimer by Benzel, Dykstra, and Vincent indicate the ground state of the dimer is a singlet state. These calculations are far more accurate than all the preceding minimal basis set calculations. Nonetheless, they do not seem to be very reliable due to the fact that the reported total energies for the dimer do not appear to us to be bound against dissociation into the separated atoms, when one uses the stated basis set for the atomic calculation. This was tested by us at the Hartree-Fock level. The available calculations agree poorly with respect to such features as bond lengths. In this respect they are in poor agreement with experiment. In order to begin our NO studies we

have initiated studies of the N_2 , the O_2 , the NO and the N_2O_2 molecules in order to develop accurate basis sets for the separate molecule fragments and for the N_2O_2 molecule, and also to determine the bond lengths and the spin type of the dimer as well as find out information about its low lying excited states. We find all interesting properties of the molecule are hypersensitive to the details of the calculation. This extends even to qualitative features. The progress will be reviewed in the next section of this report.

3. Scientific Approach and Progress in its Implementation.

The fundamental approach being pursued is the simulation of the fragment of the total solid in which the interesting phenomena occur by means of a cluster approximation. The cluster is a group of atoms or molecules plus appropriately chosen boundary potentials which simulate the entire system. Provided the phenomena one wishes to study is reasonably localized in extent this is a very good approximation. What is more, this spatially localized approximation is ideal for the simulation of such properties as chemical changes or localized excitations or impurity/defect situations. The current level of implementation is with the unrestricted Hartree-Fock approach (UHF). There is need to incorporate directly correlation effects. Presently we are employing the single reference Many Body Perturbation Theory approach (MNPT). As we will see, there are interesting problems involving N_2O_2 , which involve near degeneracies and curve crossing which require an improved approach. The one which we are choosing is the multi reference Many Body Perturbation Method (MRMBPT). This latter method has been tentatively implemented by us in a prototype way and is proving accurate but difficult to implement. Recently we have constructed an automated code to facilitate the implementation

This code is yet in its infancy. All these methods seem to be accurate in practice, but are quite intensive of computer resources if one is to achieve the desired accuracy, and do a sufficient number of calculations.

Presently we are resolving the ambiguities relating to the bond lengths and bond angles and spin state of the free NO dimer. The most accurate calculation published is due to Dykstra et al. This calculation employs the Dunning basis for the N and the O atoms, and uses d-polarization functions on the atoms. This study finds the dimer to have a 1A_1 ground state in the cis geometry with an N-N bond length significantly shorter than experiment. The ground state energy was found to be -258.470 Hy. A low lying excited state in the cis geometry is found to be in a 3B_1 state with a total energy of -258.445 Hy. a value which is nearly degenerate with the ground state. If this result is substantiated it could be significant as regards the energetic properties of NO as the decomposition of a singlet NO dimer into N_2 and O_2 is spin forbidden. A low lying triplet state would therefore greatly facilitate the decay process. We began our studies by reproducing the essential features of the Dykstra calculation. We then tried to study the stability of the answers by augmenting his basis with bond centered s-functions for the NO and NN bonds. Doing this produces significant lowering of the system energy. The 1A_1 state lowers its energy to -258.539 Hy, and the 3B_1 state is lowered to the same value. All quoted numbers are Hartree-Fock values. Inclusion of correlation energy does lower the singlet state with respect to the triplet, however, we believe that this is not a cause for complacency. Currently we are augmenting our calculation by using a double zeta basis of Huzinaga for the separate atoms. This is an improvement on the Dunning set. We are using d-polarization functions on all atoms and are using carefully optimized s and p bond centered functions in all bonds. We believe this basis

set may allow definitive answers to the geometric and the spin state questions. Currently all needed basis set development has been done and we are awaiting our time on the FPS-164 scientific computer. We expect the studies of the NO dimer will occupy the next two months. When we finish with this dimer, studies will be initiated immediately with clusters of dimers to simulate bulk and surface situations in order to ascertain the modes of energy trapping in the NO solid and hopefully to try to understand the dominant paths to instability.

4. Unexpected Funds.

There will be no unexpected funds in this grant at the expiration of the present contract period.

5. Other Support of the Principal Investigators.

Dr. A. Barry Kunz receives support as a member of the MRL at the University of Illinois from the NSF black grant to that facility. His current funding level is about \$100,000/year. The grant number is NSF-DMR-80-20250.

Dr. R. S. Weidman receives support as a member of the MMRL project at Michigan Technological University. This support comes from the NSF and is at an annual level of \$20,000/year. The grant number is NSF-DMR-81-16363.

6. Publications and Invited Talks.

1. A. B. Kunz, Study of the electronic structure of twelve alkali halide crystals, Phys. Rev. B 26, 2056-2069, (1982).
2. A. B. Kunz, Electronic structure of AgF, AgCl, and AgBr, Phys. Rev. B 26, 2070-2075, (1982).
3. A. B. Kunz, Electronic structure of solid methane, Phys. Rev. B 28, 3465-3473, (1983).

4. A. B. Kunz, Solid State Theory, The Encyclopedia of Physics, Accepted for publication.
5. A. B. Kunz, Theory of the electronic structure and optical properties of organic solids: collective effects, proceedings of the NATO ASI on Polymers: Solid State Aspects, accepted for publication.
6. A. K. Ray, S. B. Trickey, and A. B. Kunz, Optical absorption of solid Xenon at high pressure, accepted for publication.
7. D. R. Beck and A. B. Kunz, Excitation energies for the lowest triplets and the singlet-triplet splittings in the gas phase methane including many body effects. Submitted for publication.
8. A. B. Kunz, J. C. Boisvert, and T. O. Woodruff, Li K-edge Soft X-ray Absorption in LiF, submitted for publication.

Invited Lectures:

- A. B. Kunz, Localization and the Optical Properties of Metals, Joint Physics Chemistry Seminar, The University of Georgia, March 1983.
- A. B. Kunz, Strategies for Solid State Computations, Chemistry Seminar, The Johns Hopkins University, August 1983.
- A. B. Kunz, Panel on the Impact of Computers on Quantum Chemistry, Sanibel Symposium, Palm Coast, Florida, March 1983.
- A. B. Kunz, Excited States in Molecular Solids, Collective Effects, NATO ASI, Braunlage, West Germany, July-August 1983.
- A. B. Kunz, Energy Trapping Transfer and Release in Molecular Solids, DOD Workshop, Great Oaks, Maryland, August 1983.
- A. B. Kunz, The Electronic Structure of Impurities and Defects in Simple Metals; Meeting of the Metallurgical Society, Philadelphia, Pennsylvania, October 1983.

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