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PROPERTIES OF THREE-DIMENSIONAL ENERGETIC SOLIDS AND
MOLECULAR CRYSTALS; MICHIGAN TECHNOLOGICAL UNIV
HOUGHTON A B KUNZ ET AL. 1982 N00014-81-K-0620

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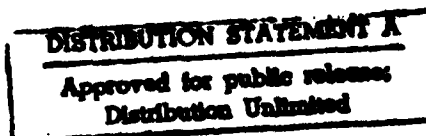
Technical Report on Grant ONR-N-00014^{SL}K-0620
Period 1 April 1982 - 31 December 1982

"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 related to energetic materials in their solid phase and also on other molecular solids which serve as prototypes. These studies are entirely theoretical in nature and are employing exclusively non-parametric ab-initio techniques.

In the case of solid fuels or explosives the area of prime concern is the initiation of combustion or detonation. This may be accomplished by means of shock, or of high temperature or both. Thus we need to be able to study these systems under extreme conditions of temperature or pressure. In order to accomplish this objective it is necessary to extend the normal solid state methods employed for studying the electronic or vibronic structures as such theories are essentially $T=0$ theories.

↑ If one is able to explain the initiation process, then it is essential to be able to explain how one might sustain the combustion as well. One likely mode of sustaining the reaction is an auto-catalytic mechanism.

Finally one need examine those properties of the solid which contribute to the stability of the system, and if possible how such properties are influenced/controlled by impurities or defects or their aggregates.

2. Partial List of Unsolved Questions of Scientific Interest.

If one is to except the solid rare gases and such inherently

one-dimensional systems as polymers, very few theoretical studies have been performed on crystalline molecular solids. The majority of the extant studies are by means of cluster simulations rather than by use of extended system techniques (such as energy band theory). In addition the majority of studies are of a partly (or even totally) empirical nature. The one current exception to this is the case of solid CH₄, which has been studied in a Hartree-Fock model some 10 years ago. Unfortunately the calculation made some unacceptable approximations to the Fock matrix elements and is not wholly reliable. This and other criticisms of the previous work are detailed in the accompanying manuscript on solid CH₄. In addition the present results extend past knowledge by including explicit treatment of correlation effects and also in that it includes the effects of hydrostatic pressure.

The fundamental theoretical knowledge of even such a simple energetic solid as NO is to all intents and purposes zero. Clearly then one does not expect (nor does one find) any detailed theoretical understanding of the fundamental processes in more complicated and more important (technologically) solid energetic systems.

3. Scientific Approach and Progress in its Implementation.

Two fundamental and complementary approaches are to be employed in this study. The first of these is applicable to systems having translational invariance is energy band theory, the second is more applicable to those systems lacking even one



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dimension with translational invariance such as systems with point defects or impurities, this being extended cluster modeling. In this latter approach the extended system is modeled by a group of molecules, twenty or so in number, which are bounded by a self-consistently determined potential to simulate the remainder of the system. This cluster is then solved self-consistently in the Unrestricted-Hartree-Fock (UHF) approximation separately for each state in question. The virtual UHF orbitals are retained and employed as a basis set for computing the correlation energy of the states in question by means of Many-Body-Perturbation-Theory (MBPT). This is not an unusual method for studies of molecular ground states, but what is unusual here is its employment on such a large system and also for excited states. In order to develop the excited state technology we have been looking at some open shell singlets. In so doing it becomes necessary to employ several projection techniques to prevent variational collapse. This is scientifically important but not yet critical to this program so that this particular study is given very low priority. None the less, early results on some atoms and small molecules indicate an ability to compute the energy of excitation from ground state singlets to excited open shell singlets to an accuracy of better than 0.2 eV.

Several useful studies on CH₄ solid have been performed using these techniques. These include a study of how the C-H bond length varies as a function of the C-C bond distance. That is, the internal rearrangements of the CH₄ molecule in the solid are studied as a function of hydrostatic pressure. This calculation

permits us to deduce several very useful parameters. These include the effective CH₄-CH₄ force law, the C-H force law and the H-H force law. To a tolerable approximation all these forces are harmonic and the essential CH₄-CH₄ force constant is quite a bit softer than any of the others. This is useful in that it permits one to partition the vibrational modes into intermolecular and intramolecular modes. This has been done and the vibronic properties of the bulk system deduced. Defects were introduced in the bulk and on the surface by removing a CH₄ molecule, and the vibrational energies recomputed. These results are interesting and we believe significant. We find that a bulk vacancy introduces a local soft mode into the vibrational structure, whereas the surface vacancy does not. Therefore we conclude that the bulk vacancy may serve as an energy trap but the surface one is not likely to do so. Clearly this point needs further study on several more interesting cases, but this suggests that the surface vacancy is not likely to act as a point for initiation of combustion if the energy transfer mode is the vibrational spectrum. Clearly we will pursue this study further and extend it to ND as soon as practical. It is intended to write up the basic results of the cluster studies for CH₄ for publication in the near future.

The implementation of ab initio energy band methods to the study of molecular solids seems to at last be a useful success. The method of choice is the linear-combination-of-molecular-orbitals (LCMO) approach for technical reasons detailed in the prior reports. The initial attempt to implement this idea was

technically a success ,but far too slow in practice to cope with solids more complex than Ar, or CH₄. Therefore with the goals of this project in mind, I determined to reformulate the entire LCMO approach to gain the necessary speed. This has been successfully completed, and a code now exists which should easily allow one to study energy bands in systems as complex as NO or even more complex. The energy band studies here are at the HF level. If one is to explain experiment or have quantitative predictive ability, the inclusion of correlation effects is necessary. There are two essential problems here, the first is that the correlation energy for a solid is infinite, but has finite differences upon excitation. Thus any attempt to evaluate the correlation energies in two states is foredoomed to failure, and one must develop techniques to evaluate the differences directly. The second problem is that of size consistency. This problem is somewhat avoided as is seen in the preliminary manuscript on solid CH₄, when one computes changes in energy rather than the energies directly. The changes are at least in part not extensive quantities as we show. Those parts which are extensive are then evaluated by means of MBPT methods. The essential interesting result for solid CH₄ is that the energy band gap is a highly sensitive function of the lattice constant. The lowest gap is indirect and has a value of 13.17 eV at normal lattice constant and decreases precipitously to 10.86 eV when the lattice constant is decreased by 5%. This suggests for narrow gap solids that pressure plus elevated temperature could excite quite a few molecules out of their electronic ground state. The utility of

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this is further seen if we include the electron-hole interaction between the excited electron and the hole left in the valence band. This interaction causes the two entities to form an exciton and this drives a local distortion of the CH₄ molecule from the ideal T_d geometry to D_{2h}. In this change one enables the separation of the CH₄ into two reactive elements, H₂ and CH₂, if one further perturbs the system. This suggests that electronic excitations may play a significant role in the oxidation of such systems. The full details of this study are attached. It is expected to pretty up a few details of the codes and then start on solid NO.