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13. ABSTRACT (Maximum 200 words)

Our experimental and theoretical objectives have focused on adamantane, the first diamondoid. This compound gives us substantial detailed information about the interaction between carbon-carbon, carbon-hydrogen, and hydrogen-hydrogen atoms. This has provided a first test case for the theoretical teams at the University of Missouri–St. Louis and Indiana State University to accurately measure and compute the electronic structure and mechanical properties. The results have been compared with the existing model potentials, through which we have been able to systematically improve the quality of those potentials. Experimental intermolecular force measurements, positional assembly and applications of diamondoids as molecular building blocks have been carried out by the experimental teams at Argonne National Laboratory and University of Illinois at Chicago.

Over 30 publications have resulted from this work, including a book on *Molecular Building Blocks (MBBs) for Nanotechnology*, published in 2007 by Springer-Verlag. This book, edited by the principal investigators for this grant, consists of seventeen chapters covering all the important aspects of MBBs, including diamondoids and the relation of diamondoids with other MBBs.

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(4) Statement of the problem studied

Our problem is to investigate the complicated structure-property relation of organic nanostructures at the nanoscale level by high-level materials simulation. A clear understanding of such a relation is extremely essential to designing functional molecular gears for micro-machines and sensitive bionanosensors. Diamondoids are excellent materials for this study.

(5) Summary of the most important results

Our theoretical investigations have progressed quite well, with the following results:

(i) Method characterization of diamondoids

Challenges to simulate nanostructured are obvious both theoretically and computationally. However, what is even more challenging is the selection of a reliable and workable theoretical method which can handle a wide range of mechanical properties of diamondoids. We have tested two different quantum chemical softwares, where one is Molpro and the other is Gaussian03. Molpro usually has faster performance than Gaussian03 for small systems at the Hartree-Fock level, but uses too much disk space and memory for a large system. We have found Gaussian03 to be more appropriate for adamantane. We have discovered that the Hartree-Fock method gives a correct molecular symmetry but a very poor mechanical property. We have found that the density functional theory at the B3LYP level gives a much better result. This is also consistent with all the previous theoretical and experimental investigations.

(ii) First-principles simulation of the interaction between adamantane and an atomic-force-microscope tip

Here we have used the first-principles calculation to investigate the interaction between adamantane and an atomic-force-microscope tip. By holding the tip at different distances from adamantane, three scans across two surfaces – one with a carbon atom at the center and the four other equivalent atoms at the corners, and the other with three equivalent carbon atoms in the front and three other atoms in the back forming a hexagon shape – reveal the detailed morphology of adamantane. For the first scanned surface, a huge potential energy change is observed when the tip is close to adamantane, which results from the strong interaction from two hydrogen atoms attached to the center carbon atom. On the second scanned surface, a radial scan shows a maximum force constant of $2 \text{ Hartrees}/\text{\AA}^2$. This is proof of the hardness of adamantane. The rotational scan along the second surface reveals a systematic change in the potential energy as the tip is moved away from adamantane. Due to the existence of two types of carbon atoms in adamantane, the original potential maxima are shifted 60° to new maxima. Between these maxima, there is a flat region. Finally, an x-y force scan over the above two surfaces is performed, where two distinctive images of hydrogen atoms are found. These results are detectable experimentally.

(iii) Chemical modification of adamantane structure

Motivated by a recent investigation showing that the nitrogen vacancy (NV) in diamond is magnetic (where one removes one carbon atom and replace another carbon atom by a nitrogen atom), we have investigated the possibility of whether nitrogen-modified adamantane shows magnetic properties. We have found that for a single NV, adamantane is not magnetic. This is true irrespective of which pair of carbon and vacancy is created. However, the gap between the magnetic and nonmagnetic ground states is quite small. This result suggests that in a thermal activated situation, the chemically-modified adamantane might show the magnetic properties. This could be useful as a magnetic and thermal sensor.

Our experimental studies have progressed well and are still underway as follows:

(iv) Optoelectronic behavior of diamondoids molecules

Diamondoids have been of great interest in recent years due to their role in nanotechnology, drug-delivery and medicine. Due to their six or more linking groups, they have found major applications as templates and as molecular

building blocks in nanotechnology, polymers synthesis, drug delivery, drug targeting, DNA-directed assembly, DNA-amino acid nanostructure formation, and in host-guest chemistry. In this project, the molecular nature of diamondoids, their molecular specificities, their intermolecular interactions and their opto-electronic properties have been studied in a combined experimental-theoretical effort. These studies are aiding in our understanding of the structure-property relations and self-assembly of diamondoids, which is essential for designing functional molecular gears for micro- and nano-electro-mechanical systems (MEMS and NEMS) and sensitive bionanosensors, and for developing new nanodrugs, just to name a few. The experimental investigations on this subject have been utilizing the facilities of the Center for Nanoscale Materials of Argonne National Laboratory.

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