

Project Title:

Computational materials Science

First-principles studies of high pressure structures between Xe and other elements.

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1. Background

The project was motivated by recent experimental discoveries of new classes of novel molecular complex at moderate pressure [1,2]. These observations have raised the speculation that new-type of chemical bonding may exist at high pressure [3]. The project is to study the structure and dynamics of selected systems using First Principles calculations and ab initio molecular dynamics simulations. In the initial study we have chosen the system of $\text{SiH}_4\text{-H}_2$. A molecular complex with stoichiometry $\text{SiH}_4\cdot 2\text{H}_2$ with face-centered cubic (FCC) structure has been found to be stable from 5 GPa to over 35 GPa. The pressure dependence of the H_2 vibrons show anomalous behavior as compared to solid H_2 under similar conditions. The objective of the project is to determine the crystal and to elucidate the vibrational dynamics. Using this information the nature of the chemical bonding can be explained.

2. Result

First Principles electronic structure calculations employing pseudopotential plane wave methods have been performed. Two public domain codes VASP and PWSCF were used for the computation. The initial positions of H_2 in the crystal structure were explored with the random search method. No satisfactory structures were found after numerous trials. An educated guess would place 8 H_2 in the octahedral sites. Geometry

optimization calculations maintaining the cubic structure resulted in an interesting structure with half of the H_2 occupying the octahedral sites and half moved to the tetrahedral sites. Only a small distortion was found even after releasing the cubic constraint. The calculated equation of states is in very good agreement with experiment. Encouraged by this result, vibrational frequencies of the system were calculated at different pressures using both molecular dynamics and linear response calculations. The results show H_2 vibrons in the two sites are different. In the octahedral site the vibrons first increase and then decrease with increasing pressure. In comparison, at the tetrahedral sites, the H_2 vibrons decrease in frequency with increasing pressure. The theoretical results are in agreement with experimental observations of two types of trends in the vibrons. However, the observed multiple Raman peaks were not reproduced by the calculations. Based on the theoretical predicted structure, the interactions between SiH_4 and H_2 were analyzed from the calculation of the natural bond orbital (NBO) [4]. It is thought that second order donor-acceptor bonding is responsible for the stability and the change in the H_2 vibrations under pressure.

3. Conclusion

Preliminary conclusions can be drawn from the theoretical results. First, it is probable that

the H₂ occupy the tetrahedral and octahedral sites. Second, donor-acceptor interaction is enhanced under pressure when molecules are pushed closer to each other. The latter conclusion may be generally applicable to other heterogeneous molecular systems under pressure.

5. Schedule and prospect for the future

The proposed project is not completed yet. Additional calculations need to be performed to investigate the origin of multiple H₂ vibron frequencies observed in the experiment. One possibility may be due to slight distortion of the unit cell. To this end, both linear response and ab initio molecular dynamics calculations will be performed. It is anticipated that the SiH₄/H₂ project will be successfully completed in the near future. A paper for publication will be prepared

6. Extension of current account

As discussed above, additional calculations are required in order to complete the initial project in a satisfactory manner. Specifically, we wish to investigate the effect of distortion of the unit cell on the distribution of the frequencies of the H₂ vibrons. Geometry optimization removing the cubic system and frequency calculations from molecular dynamics and linear response theory will be performed. After the completion of the first project, we will proceed to study two other systems mentioned in the proposal, viz, the crystalline molecular complex of Xe-H₂ [2] and Xe-Cl₂. [6]. On the latter projects, a variety of structure search techniques will be employed to explore low energy structures. Comparison of the structures and calculated vibrational spectra will be compared with experiment.

References

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Fiscal Year 2009 List of Publications Resulting from the Use of RICC

[Publication]

1. J.J. Yang, J.S. Tse and T. Iitaka, First Principles study of Liquid Lithium at High Pressure, *J. Phys. Cond. Mat.*, **22**, 095503 (2010).

