

Project Title:

Computational Materials Science

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1. Background

The projects proposed in the 2010 application dealt with the elucidation of the structure and dynamics of a new classes of novel molecular complexes synthesized at moderate pressure [1,2] discovered recently. We have chosen the $\text{SiH}_4\text{-H}_2$ for detail investigation. . This work has been completed. A second project is to identify the structures of Xe-halogen compounds under high pressure. The initial focus is the Xe-I₂ complex in which structural data is available and also has been suggested to have a metallic ground state. Other related work is on the study of the quantum phase transitions (QPT) in Cr induced by the application of high pressure The objective of the various projects is to employ first-principle methods to determine the crystal structure and elucidate the electronic and magnetic properties. From the theoretical information the nature of the chemical bonding can be obtained.

2. Computational Details

All calculations were performed on the RICC system with pseudopotential plane wave methods based on the density functional theory employing three highly parallelized public domain codes VASP, PWSCF and SIESTA codes.

3. Result

$\text{SiH}_4\text{-2H}_2$.

First Principles electronic structure calculations employing pseudopotential plane wave methods have been performed to investigate the structure and dynamics of a

recently discovered solid silane-hydrogen complex. A structure with orientationally disordered silane and hydrogen with their centers of mass arranged in a distinctive manner are found. This result is in good agreement with the experimental crystal structure. Natural bond orbital analysis revealed that perturbative donor-acceptor interactions between the two molecular species are enhanced by pressure. The unusual anti-correlated pressure-frequency dependency is reproduced from extensive constant-pressure and variable cell molecular dynamics simulations. The observed multiple Raman peaks of H₂ can be explained by temporal changes in the environment due to deviations of the lattice parameters from the ideal cubic lattice. The most significant results emerged from this study is that second order donor-acceptor bonding will be important factor to stabilize closed shell molecular complexes under pressure. We anticipated that many other systems that have been reported can be explained using this model. The results of this work had been published in Phys. Rev. Lett. and was highlighted in the January 2011 issue of RIEKN Research (<http://www.rikenresearch.riken.jp/eng/research/6495>)

Xe-I₂

Using a variety of computational techniques, a candidate low pressure crystal structure for the Xe-I₂ complex has been obtained. This space group and unit cell parameters for the theoretical structure at 7 GPa are in excellent

agreement with experiment. Moreover, this structure is found to be metallic. This finding is surprising but agrees with experiment! The structure has a highly distorted I arrangement around the Xe atoms with strong intermolecular I₂ interactions forming a chain like structure. The nature of the usual chemical bonding and structural motif are under investigation.

Cr

This work was in close collaboration with Dr. Z. Li, a postdoctoral fellow in Dr. Iitaka's group. I have written routines for the calculation of the Fermi surface and nesting vectors with the VASP code. We have identified several q-dependent spin-spiral states and the preliminary results seem to support the experimental result of a QPT near 9 GPa. We intend to submit a paper reporting our results in the near future..

4. Conclusion

We have completed the project on the study of the structure and dynamics of SiH₂-2H₂ at high pressure. Our work revealed a new mode of chemical interaction, viz, the donor-acceptor bonding between the otherwise closed shell SiH₄ and H₂ molecules. Preliminary results show a promising structure to explain the new observation of a low pressure metallic Xe-I₂ complex. Software has been developed for the calculation of the Fermi surface and nesting vectors using the VASP code.

5. Schedule and prospect for the future

The proposed projects in 2010 have not fully completed yet. Calculations and analysis are need to characterize the chemical bonding mechanism and to explain the origin of the metallic state in Xe-I₂. We also plan to expand the study to the halogen Xe complexes of H₂ and Br₂ [2]. Further investigation is planned to continue on SiH₄-H₂ with a focus on the effect of the concentration and distribution

of H₂ to the structure and vibrational properties of the complex.

6. Extension of current account

As discussed above, substantial calculations are required in order to complete the proposed projects in a satisfactory manner. Specifically, we wish to investigate the effect of distortion of the unit cell to 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. With a promising candidate structure now at hand, the priority is completed the study on the structure and properties of the Xe-I₂. We will then proceed to study two other systems mentioned in the proposal, viz, to elucidate the crystalline molecular complex of Xe-H₂ and Xe-Cl₂.

References

1. T.A. Strobel, M. Somayazulu and R.J. Hemley, *Phys. Rev. Lett.* **103**, 065701 (2009).
2. M. Somayazulu, et.al., *Nature Chemistry* **2**, 50 - 53 (2010)

Fiscal Year 2010 List of Publications Resulting from the Use of RICC

[Publication]

Yim, W.-L., Tse, J.S. & Iitaka, T. Pressure-induced intermolecular interactions in crystalline silane-hydrogen. *Physical Review Letters* , 105, 215501 (2010).

Yang, J.J., Tse, J.S., Iitaka, T, First-principles study of liquid gallium at ambient and high pressure. *J. Chem. Phys.*, submitted.

[Oral presentation at an international symposium]

Tse, J.S. "Unusual Electronic and Dynamic Structure under Pressure", 5th Asian Conference on High Pressure Research, Matsue, November 7-12, 2010.

Tse, J.S. "How Chemical Principles can be applied at High Pressure", Pacificchem, Hawaii, December 17, 2010.