

## Interactions between Metal Cations and H<sub>2</sub> Molecule: A Mini Review for Strategies of Effective H<sub>2</sub> Storage

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*Received May 23, 2018; Accepted August 30, 2018; Published January 26, 2019*

Energy is one of the key factors in deciding the social and economic development of any country. Worldwide, especially in developing countries, the energy sector has been given prime importance in view of the rapidly increasing energy demands due to the day by day improved lifestyle as well as industrial revolutions. The decreasing fossil fuel supply and climate change caused by carbon dioxide emission have spurred an initiative to develop alternative fuels. Apart from the increasing prices of the fossil fuels, their adverse effects on the environment and limited as well as depleting resources lead to the necessity of exploring new energy scenarios. Hydrogen (H<sub>2</sub>) is one of the most promising candidates for the replacement of current carbon-based energy sources [1]. Hydrogen has an energy density much greater than gasoline and emits no carbon dioxide after burning, and it has many desirable properties as a fuel. It is gravimetrically energy-dense and nontoxic, and its oxidation product is water. However, storage is difficult owing to its small volumetric density, which, coupled with challenges in production and infrastructure development, inhibits expansion of the hydrogen economy. Free H<sub>2</sub> does not occur naturally in quantity, and it should be generated from some other energy source by steam reformation of natural gas or other methods. H<sub>2</sub> is therefore an energy carrier (like electricity), not a primary energy source (like coal). For the advancement of hydrogen and fuel cell power technologies in transportation, stationary and portable application, the research on hydrogen production, delivery, storage, and fuel cell technologies should be fully developed. Over the past decade, a number of research efforts have been made to find new storage materials to achieve the established storage U.S. Department of Energy (DOE) targets [2]. Herein, a brief discussion is presented on hydrogen storage requirements, interaction between metal cations and H<sub>2</sub> molecules and the current state-of-the-art of established systems. This Review is focused on mainly the interaction between metal cations and H<sub>2</sub> molecules, which plays an important role in metal-organic frameworks (MOFs) as new hydrogen storage materials.

The interactions between metal cations and neutral molecules play important roles in hydrogen storage in porous solids and porous media, and chemical reactions in the environment. Other important applications can be found in the guiding of reactive molecular encounters occurring in the cold surroundings of interstellar space, and in driving the formation of stable non-covalent complexes in hydrogen storage materials, including MOFs and zeolites. H<sub>2</sub> is an important element used as a clean fuel for transport purposes and at the same time it is difficult to build up proper technologies for its efficient, safe, and economical storage [3,4]. At the fundamental level, H<sub>2</sub> can interact with other atoms, molecules and solids via non-covalent (van der Waals and electrostatics) and orbital interactions. Physisorption processes are reversible since no activation energy is involved and the interaction energy is very low. In materials such as MOFs, porous carbons, zeolites, clathrates and organic polymers, H<sub>2</sub> is physisorbed on the surface of the pores. In these classes of materials, the H<sub>2</sub> storage capacity mainly depends on the surface area and pore volume. The main limitation of use of these sorbents as H<sub>2</sub> storage materials is weak van der Waals interaction energy between H<sub>2</sub> and the surface of the sorbents. Therefore, many of the physisorption based materials have high storage capacities at liquid nitrogen temperature and high pressures, but their capacities become very low at ambient temperature and pressure. Research is being directed toward the synthesis of highly porous materials that would have enhanced interaction energies with gaseous H<sub>2</sub>. The positive side of

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**Citation:** Pakhira S. (2019) Interactions between Metal Cations and H<sub>2</sub> Molecule: A Mini Review for Strategies of Effective H<sub>2</sub> Storage. J Chem Sci Eng, 2(1): 41-44.

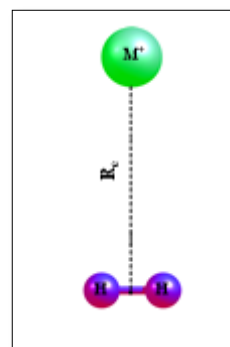
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of these kinds of porous materials is the fast adsorption and desorption kinetics.

Most interactions in bulk  $H_2$  are related to their quadrupole moment due to the non-spherical nature of  $H_2$ , so-called quadrupole-quadrupole interactions. Hydrogen gas can also interact with ions and create charge-quadrupole interaction.  $H_2$  can have an induced dipole moment and generate other interactions such as charge-induced dipole and dipole-induced dipole with a strong external field [5,6]. The other ubiquitous non-covalent interaction is due to van der Waals force which is responsible for the interaction of  $H_2$  with most molecules and materials, e.g. carbonaceous compounds such as graphite and carbon nanotubes [7]. The typical values of each of these interactions are less than 7 kJ/mol. Some general guidelines can be proposed for new potential materials for hydrogen storage. The main factors that enhance the ability of storing hydrogen in the case of physisorption are surface area, pore volume and enthalpy of adsorption. These factors can be enhanced by extended aromaticity, unsaturated metal sites and point charges in the framework of the proposed materials. The design of novel materials for hydrogen storage following the above mentioned rules has been a major task nowadays. The primary research on  $H_2$  storage has been focused on mainly the interaction between  $H_2$  and the metal ions (in the metal side) in the frameworks which plays an important role to store and accumulate the  $H_2$  gas molecules. Thus, metal cation-dihydrogen ( $M^+-H_2$ ,  $M$ =Metal) complexes are the simplest charged polyatomic weakly bound complexes having binding energies typically less than 10 kcal/mol considered for assessing computational techniques aimed at studying ion-neutral complexes that are relevant to the hydrogen storage problem. The  $M^+-H_2$  complex is the simplest one to understand the nature of intermolecular interactions between the cation and hydrogen molecule. Many scientists and researchers, some companies, governmental and non-governmental agencies, public institutions and financial institutions are convinced that the physical and chemical advantages of hydrogen will make it a significant synthetic fuel which can replace fossil fuel in near future.

Recently, Pakhira et al. [8] studied the light cation-dihydrogen ( $M^+-H_2$ , where  $M$ =Li, Na, B and Al) van der Waals (vdW) complexes (as shown in **Figure 1**) in detail using dispersion corrected double hybrid and gradient-corrected density functional (DFT-D) [8-14] methods in conjunction with correlation consistent valence triple- $\zeta$  basis set. They investigated the electronic structures, bond distance ( $R_e$ ), potential energy curves (PECs) and dissociation energy ( $D_0$ ) which agree very well with the experimental and theoretical values wherever available. The dissociation energies of  $Li^+-H_2$ ,  $B^+-H_2$ ,  $Na^+-H_2$  and  $Al^+-H_2$  van der Waals complexes calculated from the potential energy curves at mPW2PLYP-D/cc-pVTZ level are 4.83, 3.68, 2.42 and 1.25 kcal/mol, respectively, at a distances of

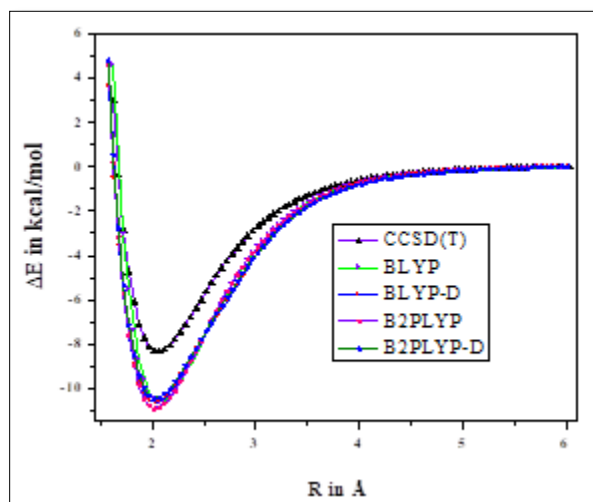
1.95, 2.25, 2.40 and 2.95 Å and these results were well harmonized with the previous experiment. Their DFT-D calculations reveal that the  $Li^+-H_2$  complex is most stable among the four cation- $H_2$  complexes, because the depth of the potential well and dissociation energy of the complex are relatively greater than that of the others. Among all these complexes,  $Al^+-H_2$  complex is comparatively less stable, as their dissociation energy as well as depth of the potential well are smaller compared to others complexes. They also computed the dissociation energy of the above mentioned vdW complexes by CCSD(T) methods and compared the values with DFT-D results. The authors applied the symmetry-adapted perturbation theory (SAPT) to quantify the nature of interactions as well as compute the individual components of the interactions energy such as electrostatic, polarization, dispersion and exchange. The SAPT results showed that the contribution of dispersion and induction were significant, although electrostatic dominates. They also computed the NBO atomic charges at mPW2PLYP-D/cc-pVTZ level of theory of the  $M^+-H_2$  complexes and the total electron density map for all the complexes were plotted by them.



**Figure 1.** Geometrical configuration and parameters of  $M^+-H_2$  ( $M$ =Li, B, Na and Al) van der Waals complexes. The dotted line represents the equilibrium bond distance,  $R_e$ , between the cation and center of mass of  $H_2$  molecule.

Sen et al. [15] carried out further investigation on the interaction between the metal cations and  $H_2$  molecule of the heavy cation-dihydrogen ( $M^+-H_2$ , where  $M$ =Mg, Ca, and Ag) vdW complexes using the same dispersion corrected and uncorrected hybrid density functional and CCSD(T) methods in conjunction with the correlation consistent triple- $\zeta$  quality basis sets for storage of  $H_2$  molecule. They computed the molecular properties, potential energy surfaces (**Figure 2**), stability, binding energy and well-depth of the metal cation-dihydrogen ( $M^+-H_2$ ,  $M$ =Mg, Ca and Ag) complexes in the gas phase. The authors claimed that the results obtained by the dispersion corrected hybrid density functional B2PLYP-D method among all other methods studied here, agree very well with the earlier experimental and theoretical results wherever available. They also estimated the different components of the interaction energy using SAPT analysis to get physical insight into the

interaction energy. The authors concluded that among the three complexes, only  $\text{Ag}^+\text{-H}_2$  is the most stable complex and it accumulates more  $\text{H}_2$  molecules as the interaction between the metal cation  $\text{Ag}^+$  and the  $\text{H}_2$  molecule is the greatest. Thus the  $\text{Ag}^+\text{-H}_2$  system stores more  $\text{H}_2$  molecule because the storage of molecular hydrogen depends on the interaction between metal cation (here  $\text{Ag}^+$ ) and  $\text{H}_2$  molecule. The  $\text{Ca}^+\text{-H}_2$  complex is the least stable as the interaction between  $\text{Ca}^+$  and  $\text{H}_2$  is the lowest and its dissociation energy is the lowest among the complexes. So, the  $\text{Ca}^+\text{-H}_2$  complex cannot store  $\text{H}_2$  molecule significantly as the binding energy of it is the lowest among all other vdW complexes.



**Figure 2.** Potential energy surfaces at different methods for the T-shaped  $\text{Ag}^+\text{-H}_2$  complex.  $R$  is the separation between the  $\text{Ag}^+$  cation and the center of mass of the  $\text{H}_2$  molecule.

Pakhira et al. [16] extended their  $\text{H}_2$  storage and interaction works of the transition metal cation-dihydrogen ( $\text{M}^+\text{-H}_2$ , where  $\text{M}=\text{Ni}$ ,  $\text{Cu}$  and  $\text{Zn}$ ) vdW complexes. They investigated the interactions between transition metal cations ( $\text{Ni}^+$ ,  $\text{Cu}^+$ ,  $\text{Zn}^+$ ) and  $\text{H}_2$  molecule in detail using dispersion-corrected and -uncorrected DFT, gradient corrected density functional (i.e., generalized gradient approximation noted as GGA), ordinary density functional and CCSD(T) methods in conjunction with the correlation consistent triple- $\zeta$  quality basis sets. They calculated the structural properties, depth of the potential well, interaction energy and dissociation energies and compared their calculated results with the previous experimental results wherever available. The dispersion-corrected DFT, mPW2PLYP-D method showed the best agreement with the experimental values. An NBO analysis was performed to understand the orbital participation in metal ligand interaction and charge transfer process in these complexes. SAPT calculations were executed to analyze the contributions of various energy components to the interaction energy. Among three

complexes, the  $\text{Ni}^+\text{-H}_2$  and  $\text{Cu}^+\text{-H}_2$  complexes are more stable than  $\text{Zn}^+\text{-H}_2$ , as their dissociation energies as well as depth of the potential wells are the greatest.

While the (strong) chemical bond is well studied, the chemistry of the very-weak interactions (i.e., vdW interactions) is far less well understood. Recent attempts to prepare hydrogen storage materials call for a better understanding of the weak “van der Waals” interactions of the hydrogen molecule with the metal cations. Charge transfer to and from the  $\text{H}_2$  molecule has an important role throughout the chemistry of physisorbed  $\text{H}_2$ . Polarization can also have a significant contribution to the physisorption of  $\text{H}_2$ , inducing electrostatic moments on  $\text{H}_2$ , and enabling an attractive electrostatic interaction with the  $\text{H}_2$  molecule. The preparation of metal sites with the proper structure, leaving the metal mostly exposed is expected to be a major experimental challenge, as these metal sites are expected to have interactions with solvent molecules that are an order of magnitude or more stronger than the interaction with  $\text{H}_2$ . interaction and charge transfer process in these complexes. SAPT calculations were executed to analyze the contributions of various energy components to the interaction energy. Among three complexes, the  $\text{Ni}^+\text{-H}_2$  and  $\text{Cu}^+\text{-H}_2$  complexes are more stable than  $\text{Zn}^+\text{-H}_2$ , as their dissociation energies as well as depth of the potential wells are the greatest.

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#### ACKNOWLEDGEMENT

S.P. thanks the SERB-DST, Govt. of India for providing the highly prestigious Ramanujan Faculty Fellowship under the Grant No. SB/S2/RJN-067/2017. S.P. is grateful to Professor Pradeep Mathur, Director, Indian Institute of Technology Indore (IIT Indore), Simrol, Khandwa Road, Indore, 453552, MP, India for supporting the research facility and encouraging me to write the manuscript. My thanks are extended to Prof. Abhijit K Das (Department of Spectroscopy, IACS, Calcutta, WB, India) who encouraged my whim of contributing to this work, and helpful discussions and guidance with computational resources. I am

grateful to all of my colleagues especially Prof. Parasharam M Shirage (MEMS, IIT Indore) and Dr. Abhijit Ghosh (MEMS, IIT Indore) for encouraging me in writing the manuscript.

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