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The relationship between activated H_2 bond length and adsorption distance on MXenes identified with graph neural network and resonating valence bond theory

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Jiewei Cheng,[1] Tingwei Li,[1] Yongyi Wang,[2] Ahmed H. Ati,[1] and Qiang Sun[1,3,a]

AFFILIATIONS

[1]School of Materials Science and Engineering, Peking University, Beijing 100871, China
[2]College of Engineering, Peking University, Beijing 100871, China
[3]Center for Applied Physics and Technology, Peking University, Beijing 100871, China

[a]Author to whom correspondence should be addressed: sunqiang@pku.edu.cn

ABSTRACT

Motivated by the recent experimental study on hydrogen storage in MXene multilayers [Liu *et al.*, Nat. Nanotechnol. **16**, 331 (2021)], for the first time we propose a workflow to computationally screen 23 857 compounds of MXene to explore the general relation between the activated H_2 bond length and adsorption distance. By using density functional theory we generate a dataset to investigate the adsorption geometries of hydrogen on MXenes, based on which we train physics-informed atomistic line graph neural networks (ALIGNNs) to predict adsorption parameters. To fit the results, we further derived a formula that quantitatively reproduces the dependence of H_2 bond length on the adsorption distance from MXenes within the framework of Pauling's resonating valence bond theory, revealing the impact of transition metal's ligancy and valence on activating dihydrogen in H_2 storage.

INTRODUCTION

One of the most promising solutions to achieving carbon neutrality is to use hydrogen energy, which has renewability and zero CO_2 emission.[1,2] However, the most difficult challenge is to find materials that can store hydrogen with large gravimetric and volumetric density and operate under ambient thermodynamic conditions.[3–5] While the bonding of hydrogen existed in nature is either too strong as in metal hydrides, or too weak as in MOFs.[6] To balance the thermodynamics and kinetics, hydrogen binding needs to be between physisorption and chemisorption, namely, in quasi-molecular form, where H_2 is activated with elongated H–H bond length.

The activation can be achieved either by electron transferring like in Kubas effect[7] or by charge polarization unveiled by Jena and co-workers.[8] The former takes advantage of the unfilled *d* orbitals of transition-metal atoms where H_2 molecules donate electrons to the unfilled *d* orbitals and the transition metals back donate the electrons to the H_2 molecules, and the latter relies on the charge polarization induced by the local electrical field. In both cases, H_2 retains its molecular bond but with stretched H–H bond length.

The H–H bond length is like a barometer that directly measures the interaction strength of H_2 molecule with materials, while the interaction directly depends on the distance of H_2 from the substrates. Therefore, it is of vital significance to explore the relation of H–H bond length changing with the adsorption distance, which motivates the studies in this direction. For example, Gründemann *et al.*[9] developed an equation based on Pauling's bond order concept and experimental evidences to explain the H–H bond length and metal-H distances' correlations in transition metal dihydrides and dihydrogen complexes. Zhou *et al.*[10] computationally studied external electric field's impact on stretching dihydrogen bond and adsorption distance on boron nitride