D$_2$ layers on MgO(0 0 1): Simulation study\textsuperscript{☆}

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\textbf{A B S T R A C T}

In response to recent helium atom scattering (HAS) and neutron scattering results, Monte Carlo simulations and perturbation theory calculations have been performed for D$_2$ on MgO(0 0 1). Monte Carlo simulations predict that D$_2$ molecules form a series of interesting structures, $p(2 \times 2) \rightarrow p(4 \times 2) \rightarrow p(6 \times 2)$, with coverages $\Theta = 0.5, 0.75, 0.83$ respectively, and followed by a formation of a top layer of $p(6 \times 2)$ unit cell symmetry. The three types of mono-layers are stable up to 13 K, whereas the top layer still exists up to 10 K. This is in partial agreement with the neutron scattering and HAS results that report $c(2 \times 2), c(4 \times 2)$ and $c(6 \times 2)$; they agree in terms of coverage and stability, but disagree in terms of symmetry. A quantum mechanical examination of the D$_2$ molecules' rotational motion shows the molecular axes are azimuthally delocalized and hence the simulated structures are c-type rather than p-type. These calculations also indicate that ortho-D$_2$ and helicoptering para-D$_2$ prefer cationic sites, while cartwheeling para-D$_2$ prefers anionic sites.

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1. Introduction

A study of the adsorbed H$_2$ and its isotopes in different rotational states on ionic crystal surfaces is of interest not only from fundamental viewpoint of understanding the gas–solid interaction but also from the technological applications that related to heterogeneous catalysis and energy storage. The adsorption of H$_2$, D$_2$ and HD molecules on ionic crystal surfaces has been studied extensively in the last twenty years using a variety of experimental techniques. Recently the adsorption of H$_2$ and its isotope D$_2$ on MgO surface was investigated using neutron scattering (NS) and helium atom scattering (HAS) techniques [1,4]. The adsorption of H$_2$/D$_2$ on MgO(0 0 1) represents a very simple system concerning the gas–solid interaction and studying the existence of quantum solid mono-layers on surfaces since those molecules are exhibiting quantum effects, owing to the light mass of the adsorbate. Early studies using neutron scattering [1], adsorption–isotherm and heat capacity measurements [2], and nuclear magnetic resonance [3] have examined the structure of sub-mono-layer films of H$_2$, HD, and D$_2$ on MgO(0 0 1) surface. The neutron scattering study found evidence of a sequence of phase transitions: $c(2 \times 2) \rightarrow c(4 \times 2) \rightarrow c(6 \times 2)$ in the D$_2$/MgO system.

This sequence was recently speculated to be existed for all three adsorbate systems (H$_2$, HD, and D$_2$) and information about the adsorbate vibration frequencies extracted using helium atom scattering [4]. However, the details of the adsorbate structure in terms of molecular positions are not directly accessible by experimental means. Therefore, theoretical and computational methods might be useful to clarify this information and set the stage for discussion the formation of a quantum solid layers of para- and ortho-D$_2$ species in adsorbed phase.

One of the methods that is useful in studying the thermodynamics properties of the adsorbed layers on solid surfaces is the Monte Carlo (MC) simulation method that yielded a reasonable results for adsorption of many different systems such as CO/MgO(0 0 1), and H$_2$/LiF(0 0 1) [5,6]. In this paper, the Metropolis Monte Carlo simulation for deuterium mono- and bi-layers on MgO(0 0 1) accompanying with perturbation theory (PT) calculation results is reported.

2. Interaction potential

To study the structure of a D$_2$ ad-layer on MgO(0 0 1) theoretically and computationally, it is necessary to construct a reasonable potentials of molecule–molecule and molecule–surface interactions. Note here the interaction potential between deuterium molecules in its ground state is approximately determined, whereas there are no potentials in any other rotational levels ($J > 0$). Therefore, classical pair potentials represent a suitable route to simulate a large numbers of molecules over the surface. The methods and potentials that applied here were explained in