A perturbation theory study of H$_2$ on LiF(001)

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Abstract

In response to recent helium atom scattering (HAS) results, Monte Carlo (MC) simulations and perturbation theory have been performed for H$_2$ on LiF(001). MC simulations predict that H$_2$ molecules form a series of structures, $p(2\times2)$, $p(8\times2)$, $p(4\times2)$ with coverages $\Theta = 0.5$, 0.625 and 0.75, respectively, that are stable up to 8 K. This is in partial agreement with the HAS results that report $c(2\times2)$ and $c(8\times2)$ structures; they agree in terms of coverage and stability, but disagree in terms of symmetry. To reconcile the results of the simulations and experiments, the orientation of the adsorbed H$_2$ molecules was studied using perturbation theory. These calculations show that the adsorbed H$_2$ molecules are azimuthally delocalized and that the structures are $c$-type rather than $p$-type. The calculations also indicate that $p$-H$_2$ and helicoptering $o$-H$_2$ prefer cationic sites, while cartwheeling $o$-H$_2$ prefers anionic sites.

Keywords: Hydrogen; Deuterium; Quantum effects; Potential energy surface; ortho-Hydrogen–para-hydrogen conversion; Monte Carlo simulations; LiF

1. Introduction

Recently, the structure of the H$_2$ adlayers on LiF(001) surface have been studied using helium atom scattering (HAS). They found that, at 8 K, H$_2$ molecules form two commensurate structures: $c(2\times2)$ and $c(8\times2)$ with surface coverages of 0.5 and 0.625, respectively [1]. The details of these structures are not directly accessible by experimental means, so theoretical and computational methods must be applied to provide this information. Previous Monte Carlo (MC) work on molecular adsorption on surfaces has yielded good agreement with experimental findings and so the same methods were used to determine details of the structures. In this paper, we report the results of Monte Carlo simulations combined with perturbation theory (PT) of molecular H$_2$ adsorbed on a LiF(001) surface.

2. Interaction potential

To study the structure of an H$_2$ adlayer computationally and theoretically it is necessary to construct molecule–molecule and molecule–surface interaction potentials. Although molecular interaction potentials exist for the $\text{CO/MgO}(001)$ system [2], but a brief summary follows. The interactions between molecules are assumed to be the pair-wise sum (over the constituent atomic sites) of the relevant electrostatic, repulsion and dispersion interactions between atoms. To model the electrostatic interactions between molecules, as well as with the surface, the H$_2$ molecule is represented as atomic point dipoles of strength 0.4174 D placed at each atomic site. These atomic dipoles are directed along the H$_2$ bond axis away from the center of mass to reproduce the experimental molecular quadrupole moment of +0.6177 D Å and yield a molecular...