

## I. INTRODUCTION

The adsorption and dissociation of  $O_2$  molecules on metal surfaces are of great importance to the subsequent oxidation reactions and to the formation of metal oxides<sup>1</sup>. This is especially true for the formation of thin oxide films that have been widely used as catalysts, sensors, dielectrics, and corrosion inhibitors<sup>2</sup>. Thus vast studies have been carried out on the  $O_2$  adsorption and dissociation on metal surfaces. During these studies, the theoretical *ab initio* modeling based on the adiabatic approximation has been proved successful over a wide range for studying the adsorption and dissociation of  $O_2$  on transition metal surfaces. By calculating the adiabatic potential energy surface (PES), it has been found that  $O_2$  molecules will spontaneously dissociate while adsorbing at reactive transition metal surfaces like iron (Fe)<sup>3</sup>. For noble transition metals like gold (Au)<sup>4</sup>, silver (Ag)<sup>5</sup>, Copper (Cu)<sup>6</sup>, platinum (Pt)<sup>4,7</sup> and Nickel (Ni)<sup>7</sup>, the adsorption of  $O_2$  turns out to depend on the ambient temperature, and both atomic and molecular adsorptions have been observed. Remarkably, in all above transition metal systems, the concept of adiabatic calculation works very well in explaining and predicting a large amount of physical/chemical phenomena during dissociation process of  $O_2$ . When the attention is focused on the nontransition metals with only *sp* valence electrons, an uncomfortable gap opens between *ab initio* prediction and experimental observation. The most notable is the long-term enigma of low initial sticking probability of thermal  $O_2$  molecules at Al(111), which has been measured by many independent experiments<sup>8,9</sup> but cannot be reproduced by adiabatic state-of-the-art density functional theory (DFT) calculations<sup>10–12</sup>. The central problem is that the adiabatic DFT calculations were unable to find any sizeable barriers on the adiabatic PES, which has led to speculations that nonadiabatic effects may play an important role in the oxygen dissociation process at the Al(111) surface<sup>11,13–18</sup>. Recently, we present a comparative study on the electronic structure of an  $O_2$  molecule in close to the Be(0001), Mg(0001) and Al(111) surfaces, and find that the triplet state of  $O_2$  is influenced by the Mg(0001) and Al(111) surfaces, but not by the Be(0001) surface<sup>19</sup>. Thus we prove that the adiabatic DFT calculations are still reliable to study the  $O_2$ /Be(0001) system, and find out sizable dissociation energy barriers for  $O_2$  molecules on the Be(0001) surface<sup>19</sup>. However, in contrast to the systematical results on the  $O_2$  dissociation on transition metal surfaces, there are still no criteria to judge whether an energy barrier is needed or whether a precursor molecular-adsorption state exists