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Ab initio reaction pathways for dissociative adsorption of dioxygen on Al (111)¹ FLORIAN LIBISCH, CHEN HUANG, PEILIN LIAO, MICHELE PAVONE, EMILY CARTER, Dep. of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ — We investigate the interaction of dioxygen with a clean aluminum (111) surface. The theoretical description of this fundamental process is challenging due to the discrete, abrupt charge transfer (CT) from the metal surface to the molecule. Indeed, experimental investigations suggest a sizeable activation barrier not accounted for by a conventional DFT description, due to exchange-correlation functional errors. We adopt a different approach, embedding a small (12 atoms) aluminum cluster in a DFT-derived potential simulating the remainder of the Al surface. The interaction between this embedded cluster and an approaching O_2 molecule is treated using high-level correlated wave function methods (CASSCF, CASPT2) that allow for a correct description of the CT process involved. We map out the potential energy surface (PES) as a function of dioxygen bond length, orientation, and position. In agreement with experiment, we find an activation barrier of ~ 500 meV, which corresponds primarily to the cost to induce CT. Additionally, the PES is consistent with oxygen abstraction as the dominant process in the case of incident perpendicular orientation, confirming the mechanism proposed to explain the surprisingly large fraction of single oxygen atoms found in STM measurements.

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