

H₂ Hindered Rotation and Ortho-Para Conversion on Pd(210)

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H₂ has a total nuclear spin $I=0$ or $I=1$ for even and odd values of its angular momentum J , respectively. In the lowest energy states, $I=1$ species, called ortho-H₂ is associated with the 3-fold ($J_z = -1, 0, 1$) degenerate anti-symmetric spin eigenfunctions, while $I=0$, called para-H₂ has a symmetric spin eigenfunction. Far away from the surface, and in the absence of external perturbations, the rotational energies for different values of J can be readily calculated as $E_J = BJ(J+1)$, (B is the rotational constant) which is equal to 0 for $J=0$ (para) and 14.7 meV for $J=1$ (ortho). When H₂ is adsorbed molecularly on a surface, its rotation becomes hindered and the degeneracies of the $J>1$ states are lifted. The surface-molecule interaction that hinders the rotational motion results in bound species that desorb at different temperatures, usually measured by temperature programmed desorption (TPD) and other similar experiments.

In terms of adsorption, H₂ is found to dissociate spontaneously on most transition metal surfaces and chemisorption is only restricted to stepped surface facets[1-3]. Further, previous studies[2,3] have shown that H₂ behaves as a quantum two-dimensional (2D) rotor on Cu(510) due to relatively large perpendicular anisotropic potential on this surface. In this study, we investigate H₂ adsorption on Pd(210) surface with the emphasis on the nuclear spin species separation and conversion using a combination of density functional theory (DFT)-based and model Hamiltonian calculations. It is known that molecular hydrogen adsorption on stepped Pd(210) is only possible after the accumulation of H atoms on the surface[4]. Our results show that H₂ molecule favors adsorption on top of Pd atoms located at the step-edge regardless of orientation and atomic H coverage. Further, we find that H₂ adsorbed in parallel orientation (defined as parallel to the $[\bar{1}\bar{2}1]$ -[001] plane of the unit cell) with respect to the surface has higher adsorption energy compared to the one adsorbed perpendicularly at low atomic H coverage ($\Theta < 3\text{ML}$). From these molecular orientation-dependent adsorption energies, we obtain the anisotropy potential that hinders rotation of H₂ on the surface and calculate its rotational state energies. We also find that ortho-hydrogen has higher desorption energy compared to para-hydrogen [5]. Using 2nd order perturbation theory, we calculate the conversion probability from ortho to para hydrogen adsorbed on the surface. We find that the hydrogen molecule adsorbed perpendicularly tend to have higher conversion probability than the parallel-oriented H₂.

References

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