Formation of weakly bound, ordered adlayers of CO on rutile TiO_2(110): A combined experimental and theoretical study

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The adsorption of CO on the rutile TiO_2(110) surface was investigated using He atom scattering (HAS), high resolution electron energy loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS), and different types of *ab initio* electronic structure calculations. The experimental and theoretical results allow to put forward a consistent picture for this rather complicated adsorbate system. At 70 K a (2×1) adlayer with a glide symmetry plane is formed, containing two molecules per unit cell which are tilted in alternate directions by about 20° relative to the surface normal. For this high density phase, the theoretical calculations reveal a substantial repulsion between CO molecules on neighboring lattice sites, in accord with the results of a detailed analysis of the experimental TDS data. The CO binding energy depends strongly on coverage and varies between 0.20 eV for the saturated monolayer and 0.36 eV for isolated molecules. The CO–CO repulsion leads to the desorption of about half of the CO molecules above 70 K and the formation of low density phases. HAS gave no indication of ordered adlayers at these lower coverages. For the internal stretching vibration of the CO molecules a value of 273 meV was determined by HREELS, in very good agreement with the theoretical calculations. [DOI: 10.1063/1.3098318]