

First Principles Calculation of the Adsorption, Diffusion and Dissociation of the CO Molecule on the Iron (100) and (111) Surface

- D.C. Sorescu (U. S. Department of Energy), E.F.C. Byrd, M.M. Hurley, and C.F. Chabalowski (U.S. Army Research Laboratory)

First-principles pseudopotential plane wave calculations based on spin-polarized density functional theory (DFT) and the generalized gradient approximation (GGA) have been used to study the adsorption of CO molecules on the Fe (100) and (111) surfaces. On the (100) surface, the most stable configuration corresponds to a 4-fold state in which a CO molecule is tilted relative to the surface normal by 50° . In this case, the CO bond is elongated to 1.32 Å and has a low vibrational stretching frequency of 1246 cm^{-1} relative to the experimental gas phase value of 2170 cm^{-1} . The adsorption energy for this state is found to vary between 46.7 and 43.8 kcal/mol depending on the choice of exchange-correlation functional used in the DFT. A total of three adsorption sites have been located, and the relative adsorption energies are $E(4\text{-fold}) > E(2\text{-fold}) \approx E(1\text{-fold})$ at lower surface coverage, and $E(4\text{-fold}) > E(1\text{-fold}) > E(2\text{-fold})$ at higher coverage. A similar analysis performed for the C and O atoms indicates that the adsorption at the 4-fold site is the most stable among various configurations, with adsorption energies of 186 kcal/mol and 145 kcal/mol, respectively. The minimum energy pathways for the surface diffusion of a CO molecule on the (100) surface between selected pairs of local minima indicate that the barriers for these processes are generally quite small with values typically on the order of a few kcal/mol. One exception to this is the diffusion out of the most stable 4-fold site, where the barrier is predicted to be around 13 kcal/mol. Finally, the barriers for dissociation of CO bound in a 4-fold site have been calculated to have values in the range of 24.5-28.2 kcal/mol, supporting the experimental observation that dissociation of CO bound to the surface seems to compete with CO desorption at 440 K. Similar results will be presented for the diffusion and dissociation pathways on the (111) surface.