Infrared spectroscopy of physisorbed and chemisorbed N-2 in the Pt(111)(3x3)N-2 structure

Using infrared spectroscopy and low electron energy diffraction, we have investigated the adsorption of N-2, at 30 K, on the Pt(111) and the Pt(111)(1x1)H surfaces. At monolayer coverage, N-2 orders in commensurate (3x3) structures on both surfaces, and we propose that the unit cells contain four molecules in each case. The infrared spectra reveal that N-2 exclusively physisorbs on the Pt(111)(1x1)H surface, while both physisorbed and chemisorbed N-2 is detected on the Pt(111) surface. Physisorbed N-2 is the majority species in the latter case, and the two adsorption states show an almost identical uptake behavior, which indicates that they are intrinsic constituents of the growing (3x3) N-2 islands. An analysis of the infrared absorbance data, based on a simple scaling concept suggested by density functional theory calculations, supports a model in which the (3x3) unit cell contains one chemisorbed molecule in end-on atop configuration and three physisorbed molecules. We note that a classic “pinwheel” structure on a hexagonal lattice, with the end-on chemisorbed N2 molecules acting as “pins,” is compatible with this composition.