

Investigation of Methyl Radicals on the Rh (111) Surface

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Vibrational studies of methyl on Rh(111) show a softened C-H stretching mode which is shifted by over 200 cm^{-1} . A possible reason for this phenomena is that methyl prefers a tilted geometry which increases the interaction of one C-H bond with the surface. Using density functional theory, we have investigated the energetics of methyl tilting on this surface. We first computed the binding energies at three different surface sites (fcc, hcp and top). Our results show that adsorption is preferred at the fcc hollow site. Furthermore, of the two possible molecular orientations (C-H bonds aligned with atoms or bridge sites) we find that C-H bonds prefer to point towards rhodium atoms by over 0.5 eV. We next investigated the possibility of movement away from a three-fold symmetric structure by computing the binding energy for various translations and tilting of the methyl radical. In all cases studied, methyl radicals prefer a symmetric structure on the surface and therefore can not be responsible for the softened C-H stretch.