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Surface vibrations of adsorbates on Si(111): From small clusters to infinite lattices

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Organic functionalization of semiconductor surfaces is a growing research area that offers the possibility of molecular level control of surface features and tailored electronic properties. In this work, quantum chemical cluster calculations are used in conjunction with surface vibrational spectroscopy to determine the structures of functionalized Si(111) surfaces. Interestingly, the interpretation of these spectra even for simple adsorbates is not straightforward. In the limit of high coverage, most calculations using small cluster models lack the long range coupling of the real surface that is required to make definitive assignments. In order to understand the relationship between clusters and infinite periodic vibrations, we have investigated the geometries and harmonic vibrational frequencies of the methyl, acetylenyl, methylacetylenyl, hydrogen, deuterium and chlorine functionalized Si(111) surfaces. From a careful analysis of these systems, we have derived a technique where the collective vibrational modes corresponding to the vibrations of the infinite periodic system can be derived from relatively small cluster models. The calculated frequencies are in good agreement with available experimental values and yield novel insights about the coupling between low frequency adsorbate frequencies and surface phonons. The efficacy of this approach for surfaces of varying adsorbate coverage and the prediction of novel frequency shifts will be discussed along with more complex systems.