Structural, Vibrational, and Electronic Analysis of Titanium-Carbide Nanocrystals

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Stable transition-metal carbide nanocrystals were first observed experimentally in the early 1990's. The most abundant, and presumably most stable, species is the 3×3×3 nanocrystal, $Ti_{14}C_{13}$. Using density functional theory in the generalized gradient approximation, we have carried out a systematic and comprehensive theoretical analysis of the structural, vibrational, and electronic properties of this system. For every occupied molecular orbital and several of the low-lying unoccupied molecular orbitals, we have computed the energy, symmetry label, and best-fit decomposition into combinations of atomic orbitals. To assist in the analysis and visualization, we developed a technique for transforming all electronic Kohn-Sham wave functions from complex to real and, in the case of degenerate states, for rotating to a basis that manifestly exhibits the symmetry of the degenerate subspace. For every vibrational mode of the system, we have computed the frequency, symmetry label, and atomic displacement pattern; and for infrared-active vibrations, we have also calculated the IR absorption strength. The resulting infrared spectrum is in good agreement with the experimental data.