Molecular conformation of chemisorbed molecules on metal nanoparticles and nanostructured materials plays a major role in many applications of nanotechnology. Vibrational Sum Frequency Generation (VSFG) spectroscopy was used to study the nanoscale geometric effects on molecular conformation of 1-dodecanethiol ligand on gold and silver nanoparticles of varying size between 1.8 nm and 25 nm. By analyzing the CH$_3$ and CH$_2$ stretch transitions of 1-dodecanethiol using the spectroscopic propensity rules for the 2$^{nd}$ order VSFG process, we observe the increase of the gauche-defects in the alkane chain of the ligand on the nanoparticle surface when the curvature approaches the size of the molecule (1.6 nm). In contrast, linear infrared absorption spectra, governed by different selection rules, do not allow observation of the size-dependent conformational changes. The results are understood in terms of the geometric packing effect, where the curvature of the nanoparticle surface results in the increased conical volume available for the alkane chain.