Unraveling molecular dynamics at interfaces is important for understanding surface reactivity, cell membrane dynamics, and the formation of hydrogen bonds. Up to now, details of the rotational molecular dynamics were overlooked in most vibrational SFG studies. Here we investigate molecular orientational dynamics at the air/water interface on a model system, a propiolic acid rigid rod molecule. We measured SFG signals from the C≡C triple bond stretch with various input and output polarizations. The most spectrally narrowed lineshape for SSP polarization mostly represents the vibrational dynamics, while spectrally broader SPS polarization is more sensitive to the in-plane orientational dynamics. Our model system based on propiolic acid at the air/water interface demonstrates the in-plane rotation of propiolic acid within the dephasing time scale (~1 ps). In a remarkable contrast, similar carboxylate groups in bulk water show significantly longer re-orientation times (7-18 ps), presumably due to the significant difference in H-bonding interactions at interfaces and bulk for small molecules.