The vibronic, photoionization efficiency, and cation spectra of 3,5-difluorophenol have been recorded by using the resonant two-photon ionization and mass-analyzed threshold ionization techniques. The distinct spectral features mainly result from the in-plane substituent-sensitive bending and ring deformation vibrations of these species in the electronically excited $S_1$ and cationic ground $D_0$ states. Comparing these results with those of previously reported 2,4-difluorophenol, 2,5-difluorophenol, and 3,5-difluorophenol, we gain knowledge about the substituent effect on the transition energy and molecular vibration of these positional isomers.