Estrone, estradiol, estriol are known as endogenous estrogen which have the same steroidal frame with different substituent, leading to difference of physiological activity upon the formation of hydrogen bond with estrogen receptor. In the present study, structures of estrogens and their hydrated clusters in a supersonic jet have been studied by various laser spectroscopic techniques and density functional theory calculation to study how the difference of substituents affects their hydrogen bonding ability. Infrared spectra in the OH stretching region indicate a formation of intramolecular hydrogen-bond in estriol, which may lead to weaker physiological activity among the three estrogens. We also measured electronic and infrared spectra of 1:1 hydrated clusters of estrogen. The results show a switch of stable hydration site from the phenolic OH group to the five member ring by substituting one more OH group.