TFE is an important organic solvent. TFE and water are often used as co-solvents in the studies of protein folding process. Therefore it is very important to understand the interactions of TFE with water and itself in great detail. We have studied the complexes of TFE with water and with itself using high level ab-initio calculations and rotational spectroscopy. Broadband rotational spectra of TFE and TFE+water in helium have been obtained using a chirped pulse Fourier transform microwave (FTMW) spectrometer. The rotational spectra of the lowest energy conformers of the TFE-water complexes and the TFE dimer are assigned for the first time. The final frequency measurements have been done with a cavity based FTMW spectrometer. Some interesting tunnelling splittings have been observed in the rotational spectra of the TFE-water complex. Extensive isotopic studies of H2O, D2O and DHO have also been performed to get more insight into the tunneling motion and structure of the TFE-water complex.