An $^2\text{H}/^1\text{H}$ isotope shifts in the $^1\text{H}$ NMR spectra of water in gaseous environment of fluoromethanes

Włodzimierz Makulski
Department of Chemistry, Warsaw University
02-093 Warsaw, Pasteura 1, Poland

In the present study the measurements of $^1\text{H}$ chemical shifts in $\text{H}_2^{16}\text{O}$ and $\text{H}^{16}\text{OD}$ molecules in gaseous mixtures with fluoromethanes are discussed. Over the range of accessible pressures of the gaseous buffer used the proton chemical shift vs. density of the medium relation is linear for either isotopomer and can be subjected to linear regression analysis. The analysis allowed to find the proton shielding constants in isolated HOH and HOD molecules at 300K. The isotope effect associated with this shielding, $^2\Delta\sigma(^2\text{H},^1\text{H})$, was evaluated to be 0.0386 ppm and this value was compared with the available literature data. The new result for the isotope effect shows a better fit to the results obtained by the \textit{ab initio} calculations [1], than the experimental data thus far known for liquid phase [2-4]. Obviously, for the strongly polar water molecules the interactions in liquids are very strong and significantly affect the $^1\text{H}$ shielding parameters. Thus measurements in gaseous solutions proved expedient, with extrapolation of the results to a zero pressure. The effect of molecular interactions in the $\text{CF}_n\text{H}_4n$/HOH/HOD systems on the shielding of protons of water in the gaseous complexes formed were discussed. The spin-spin coupling $^2J(^2\text{H},^1\text{H})= -1.06$ Hz was measured experimentally in the partly deuterated water in gas phase for the first time. The adequate $^2J(^1\text{H},^1\text{H})$ coupling constant in HOH found on this basis is -6.89 Hz.

Fig.1. 500MHz $^1\text{H}$ NMR spectrum of HOH/HOD in gaseous CH$_3$F at 300K.

References: