NMR CHEMICAL SHIFTS AND SPIN-SPIN STUDIES OF ETHANE, ETHYLENE, ACETYLENE AND ACETONITRILE IN THE GAS PHASE

Marcin Wilczek

In this study, there are presented the measurements of NMR chemical shifts and scalar spin-spin couplings performed for molecules of $^{13}$CH$_3^{13}$CH$_3$, $^{13}$CH$_2^{13}$CH$_2$, $^{13}$CH$^{13}$CH, $^{13}$CH$_3^{13}$CN and CH$_3^{13}$C$^{15}$N in the gas phase. The results obtained at 300 K allowed for the determination of the nuclear shielding constants for isolated molecules ($\sigma_0$) and the $\sigma_{(A-B)}$ parameters responsible for the dependence of nuclear shielding on density in gaseous matrices. In numerous experiments it was confirmed that the spin-spin couplings were also linearly dependent on density. It permitted the evaluation of the $J_0$ coupling constants for isolated molecules and the $J_{(A-B)}$ parameters which described the dependence of spin-spin coupling on density. The experimental values of $\sigma_0$ and $J_0$ remain in good agreement with appropriate ab initio data taken from literature, especially when the theoretical results include rovibrational corrections calculated at least at the zero-point vibration (ZPV) level. As an example the excellent agreement between experimental and theoretical spin-spin couplings for an acetylene molecule is presented. It is interesting that the dependence of $^1$H and $^{13}$C shielding on density is gradually increasing from ethane to ethylene, acetylene and acetonitrile. Let us note that the last compound consist of molecules with large electric dipole moments (3.9 D). The similar dependence of shielding observed for nuclei of methyl groups has revealed the influence of kinetic factors on the $\sigma_{(A-B)}$ parameters (the position of methyl group relative to the center of molecular mass - “site factor”). It was also observed that spin-spin couplings were always changed with density of gas in the same direction as it was observed in liquids.