Experimental Gas Phase ^{1}H NMR Spectra and Basis Set Dependence of *ab initio* GIAO MO Calculations of ^{1}H and ^{13}C NMR Absolute Shieldings and Chemical Shifts of Small Hydrocarbons

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High-resolution gas phase measurements of ^{1}H NMR spectra at 400 MHz and atmospheric pressure of seven small hydrocarbons are presented. The developed new method and the experimental set-up are described. *Ab initio* GIAO MO calculations of ^{1}H and ^{13}C NMR absolute shieldings on the HF, MP2 and B3LYP levels using 25 standard gaussian basis sets are reported for these hydrocarbons, based on experimental r_e distances. The measured gas phase ^{1}H chemical shifts have been converted to an absolute σ_0 shielding scale by use of the literature shielding of methane. These and gas phase ^{13}C literature values have been transferred with literature ZPV data to estimated σ_e^{exp} shieldings which are used to evaluate the basis set dependence of the calculated σ_e shieldings utilizing linear least squares regressions. Exponential extrapolations of Dunning basis set calculations allow the determination of basis set limits for ^{1}H and ^{13}C shieldings.

^{1}H and ^{13}C chemical shifts have been derived from the HF calculated shieldings with shieldings of TMS which has been geometry optimized and GIAO calculated in each basis. Standard deviations (*esd*) as low as 0.09 ppm for ^{1}H and 0.76 ppm for ^{13}C calculations have been obtained.

The statistically best basis set for simultaneous calculation of ^{1}H and ^{13}C absolute shieldings or relative shifts is 6-311G* within the HF and B3LYP methods. Aiming for highest accuracy and precision, ^{1}H and ^{13}C have to be treated separately. In this case, best results are obtained using MP2/6-311G** or higher for ^{1}H shieldings and MP2/cc-pVTZ for ^{13}C shieldings.

Key words: Experimental Gas Phase ^{1}H NMR Measurements, GIAO MO Calculations, Basis Set Dependence, ^{1}H and ^{13}C Absolute Shieldings and Chemical Shifts, Extrapolations with Dunning Basis Sets