EXPERIMENTAL AND THEORETICAL DETERMINATION OF THE ^{1}H AND ^{13}C SHIELDING TENSORS IN METHYL HALIDES

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The nuclear shielding tensor appearing in the NMR spin Hamiltonian can be divided into isotropic and anisotropic parts. The anisotropy of the nuclear shielding can be determined using NMR spectroscopy and liquid crystalline (LC) solvents; that is by varying the orientational order of the solute molecule and measuring the corresponding change in chemical shift. The orientation parameters needed for the analysis are obtained from the observed dipolar couplings. However, the contribution to the experimental dipolar couplings arising from the anharmonic [1] and harmonic [2] molecular vibrations and deformation [3] together with the anisotropy of the indirect couplings (J^{aniso}) [4] and possible complex formation [5] should be considered to get reliable results.

In this project ^{1}H and ^{13}C shielding tensors were determined for the series of methyl halides, CH_3X (X = F, Cl, Br or I). The experimental values were obtained by performing NMR experiments both in gas phase and using liquid crystalline solvents. The gas phase measurements were performed in several different pressures and the results were extrapolated to zero pressure to obtain shielding constants for free molecules. To deduct the solvent effects and to improve the accuracy of the LC experiments, two different liquid crystals and their mixture were used as solvents, measurements were carried out in various temperatures with internal reference (CH_4). Each NMR spectrum was analysed using the PERCH software [6] and the program AVIBR [1] was utilised to correct the measured dipolar couplings for harmonic and anharmonic vibrations. The experimental values are compared to the computational results (MCSCF [7] and DFT[8]).

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