Nuclear magnetic dipole moments from NMR spectra - theory and experiment

Andrej Antušek[a], Karol Jackowski[b]

Michał Jaszuński[a], Włodzimierz Makulski[b] and Marcin Wilczek[b]

a) Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland

b) Department of Chemistry, Warsaw University, Warsaw, Poland

Some of the standard literature values of nuclear magnetic dipole moments are based on old NMR experimental data. However, in the procedure used to extract the magnetic moments of bare nuclei from the NMR spectra of molecules the effects due to the shielding of nuclei by electrons have been treated in a very crude manner.

What is needed to obtain a precise value of the nuclear dipole moment is an accurate absolute shielding scale - nowadays derived from state-of-the-art ab initio calculations for a small reference molecule - and the measured chemical shift for the nucleus of interest between the reference molecule and the sample. We present an analysis combining the relevant ab initio data and experimental NMR gas-phase results. The gas-phase shielding constants are particularly useful, since they permit a direct comparison of theory and experiment, eliminating all the problems related to intermolecular interactions.

The improvements in nuclear magnetic dipole moments are most clearly demonstrated considering a relation between the shielding of different nuclei in different molecules. We have tested this relation applying the old and new values of the nuclear moments, and the shielding constants derived using the old values are meaningless. For instance, for $\sigma(^{13}C)$ in TMS we obtain 246.0 ppm, in contrast to the best present estimate, 186.44 ppm. Tracing the source of the problem we find that the magnetic moment of ^{13}C, 0.7024118 μ_N, was derived from NMR of liquid CH_3I. With the present-day values of $\sigma(^{13}C)$ and $\sigma(^{1}H)$ in CH_3I we obtain for the magnetic moment of ^{13}C 0.7023715 μ_N; combining our new experimental data for CH_4 with literature or our own ab initio shielding constants we find 0.7023694 and 0.7023698 μ_N, respectively. The latter three values lead to $\sigma(^{13}C$ in TMS) in the range 186.3—189.3 ppm, in much better agreement with 186.44 ppm. We obtain similar improvements in consistency reconsidering the magnetic moments for many other nuclei, for example ^{13}C, ^{14}N, ^{15}N, ^{17}O, ^{19}F, ^{31}P and ^{33}S [1].

[1] A. Antušek, K. Jackowski, M. Jaszuński, W. Makulski, and M. Wilczek. *Chem. Phys. Lett.*, 411:111, 2005.

e-mail: michaljz@icho.edu.pl