Nuclear Magnetic Shielding and Spin-spin Coupling Constants for Acetaldehyde from Gas-phase NMR Spectroscopy

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Experimental NMR spectrum of a measured substance provides valuable information on the chemical environment of the NMR-active nuclei in the molecule. The chemical shift observed reflects not only the nucleus position in a given molecule but also the solvent effects. In addition, the coupling constants determined from the spectra reveal information on the spatial structure of the molecule. Gaseous systems are studied in relatively ”isolated” environments, where the effects due to solvent interactions can be restricted or completely eliminated [1]. It is obvious that gas-phase NMR spectra prove useful when parameters independent of intermolecular interactions are of interest [2]. These can be used as verification of *ab initio* calculations [3,4]. Recently we provide those kind of measurements on volatile organic substances like: CH_3F, CH_3OCH_3, CH_3CN, CH_3NH_2 and CH_3OH.

This work is concerned with acetaldehyde molecule. Acetaldehyde was studied by high-precision ^{1}H and ^{13}C NMR spectroscopy in liquid and gaseous states at 300K. The gas pressure at room temperature of pure compound reached about 1 atm value but very effective relaxation processes in this conditions lead to relatively wide signals. The same signal can be substantially narrower when another component is used as a solvent to increase significantly the total pressure of the sample. To achieve this effect, approximately 0.1 mg of acetaldehyde was introduced into the buffer gases: CO_2, Xe and SF_6 taken at 0.2 – 1.3 mol/L densities. Extrapolation of the gas-phase chemical shifts to the zero-density limit permitted the determinations of ^{1}H and ^{13}C absolute nuclear magnetic shieldings of an isolated acetaldehyde molecule. The values found are shown in Table 1; additionally previously measured ^{17}O data is included [5].

Table 1: ^{1}H,^{13}C and ^{17}O nuclear magnetic shielding constants for acetaldehyde from gas phase measurements at 300K [ppm]

Group	^{1}H	^{13}C	^{17}O
$-CH_3$	28.82	156.7	
-CHO	21.03	- 7.6	- 340.0

These new experimental results are necessary in a correct verification of *ab initio* calculations of proton and carbon nuclear magnetic shieldings in the molecule under study. The indirect spin-spin coupling constants were extracted from experimental spectra and compared with the values previously reported in the literature. Intermolecular effects in the gaseous state as well as in passing from gas to liquid are also found. The gas-to-liquid shifts measured are negative both for proton and carbon nuclei showing the deshielding effect.

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