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An $^2H(D)$ isotope shift in the ^1H NMR spectra of water in gaseous environment of fluoromethanes ☆

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Abstract

Measurements of ^1H chemical shifts in $H_2{}^{16}O$ and $HD^{16}O$ molecules in gaseous mixtures with excess of fluoromethanes CH_nF_{4-n} with $n \leqslant 4$ have been obtained. Over the range of accessible pressures of the gaseous buffers used at room temperature the proton chemical shift vs. density of the medium relation are linear for either isotopomer and can be subjected to linear regression analysis. This analysis allowed to find the proton shielding constants in isolated water molecules. The isotope effect associated with this shieldings $^2\Delta^1H\ (^{2/1}H)$ was evaluated to be 0.0386 ppm and the value was compared with the available literature data. The new result for the isotope effect shows a better fit to the results obtained by the *ab initio* calculations, than the experimental data thus far known for liquid phase. Obviously, for the strongly polar water molecules the interactions in liquids are very strong and significantly affect the ^1H shielding parameters. Thus measurements in gaseous solutions proved expedient, with extrapolation of the results to a zero pressure. The effect of molecular interactions in the $CH_nF_{4-n}/H_2O/HDO$ systems on the shielding of protons of water in the gaseous complexes formed were discussed. The spin–spin coupling $^2J(^1H,^2H)$ was measured experimentally (−1.06 Hz) in the partly deuterated water in gas phase for the first time. The coupling constant $^2J(^1H,^1H)$ found on this basis is −6.89 Hz.

Keywords: ^1H NMR spectra; Isotope effects; Chemical shifts; Gas phase; Intermolecular interactions

1. Introduction

Recent years have seen a considerable rise in accuracy of the quantum-mechanical calculations of the NMR parameters by the *ab initio* approaches [1]. The calculations are primarily concerned with the shielding constants (σ) for individual nuclei and with the scalar coupling constants between them (J). They are also applied to the isotope effects observed for these constants and related to the isotope exchange of at least one of the nuclei in a molecule. A vast number of computational approaches and their variants available are responsible for the obvious necessity of their experimental verification. The water molecule is undoubtedly an attractive, yet difficult, object of interest for studies by NMR spectroscopy. The presence of a diversity of isotopes of hydrogen (H, D, T) and of oxygen ($^{16,17,18}O$) provides access to a number of isotopomers; however, low natural abundance of some of them offers an added complexity to the measurements and makes isotope enrichment indispensable.

The purpose of this work were the measurements of chemical shifts $\delta(^1H)$ in H_2O and HDO water molecules and of their associated isotope effect. The experiments to date, as being carried out in organic solvents, display considerable deviations from the results of advanced quantum-mechanical calculations. A correct assessment of these values necessitates the measurements in liquid to be compared with those made in gas phase. Low concentration of water ($<5 \times 10^{-3}$ mol/L) in mixtures with gaseous methane CH_4 and its fluorinated derivatives: CH_3F, CH_2F_2, CHF_3 and CF_4, prevents the formation of hydrogen bonds

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typically present in aqueous solutions. The stopping of the H and/or D exchange among water molecules in chemical systems has thus far been accomplished either by the application of a low, strictly controlled, water concentration in low-basicity organic solvents like acetone [2], nitromethane [3,4] or by a significantly raised temperature and a study of water in gas state [5]. In this work the conditions required were achieved by a study of the systems in the gas phase.

2. Materials and methods

Five series of gas mixtures were prepared in a vacuum apparatus at an elevated pressure, the main component of which was one of the fluoromethanes of interest, *viz.*, CH_4 (99.+%, Aldrich), CH_3F (98%, ABCR), CH_2F_2 (99.7%, Aldrich), CHF_3 (98.+%, Aldrich), CF_4 (99.9%, Aldrich). Water, of a concentration of $<5 \times 10^{-3}$ mol/L, was taken from a liquid $H_2{}^{16}O/D_2{}^{16}O$ (1:3) mixture. Triply distilled H_2O and D_2O (99% D, Aldrich) water was used. HDO was produced by mixing H_2O with D_2O isotopomer; equilibrium constant $K \sim 4$ [6]. Glass ampoules, $\varphi_{\text{ext.}} =$ 4 mm and ca. 45 mm long, of a capacity of ca. 0.16 ml, were successively filled with water and with gaseous CH_nF_{4-n} purified by freezing at a liquid-nitrogen temperature and sealed off under vacuum. For the spectrometric measurements the ampoules were placed in a standard NMR tubes of $\varphi_{\text{ext.}} = 5$ mm (Wilmad, PP 528); liquid toluene-d_8 used as external field B_0 stabilization and as a secondary reference for chemical shift (regarding neat TMS) was accommodated in the annular space. The ^1H spectra (under standard parameters) of the gaseous mixtures were recorded using a Varian 500 Unity Plus model NMR spectrometer at the Laboratory of NMR Spectroscopy, Department of Chemistry, Warsaw University.

3. Results and discussion

Observation of the proton resonance line in ^1HDO is confined to the systems in which the rapid H/D exchange connected with the presence of hydrogen bonds can be effectively stopped. This condition was realized in this study by resorting to examination of the system in gas phase. Fluoromethanes were taken for the study, as they have suitable miscibility with water at ambient temperature.

The chemical shift (δ) values for H_2O/HDO system as a function of gaseous sample density (ρ) are shown in Fig. 1. They can be seen to follow a linear relation to meet satisfactorily the linear equation:

$$\delta = \delta_o + \delta_1 \rho \quad (1)$$

which holds good for low gas pressures. The equation can be transformed into the nuclear magnetic shielding scale (σ) form:

$$\sigma = \sigma_o + \sigma_1 \rho \quad (2)$$

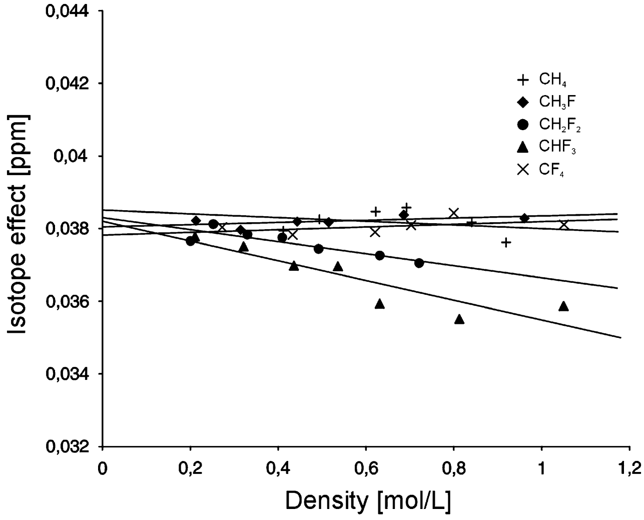

Fig. 1. ^1H nuclear magnetic shifts of H_2O and HDO isotopomers as a function of density at 300 K in the gaseous environment of methane CH_4 and its fluorinated derivatives: CH_3F, CH_2F_2, CH_3F and CF_4; measured relative to external liquid TMS.

considering that both scales are closely related thus: $\delta = \sigma_{\text{ref}} - \sigma$, where σ_{ref} denotes the shielding constant for the signal of the reference (liquid TMS). The σ_1 coefficient accounts for molecular interactions $(\sigma_1)_{\text{int}}$ and bulk magnetic susceptibility of the solution σ_{1b}:

$$\sigma_1 = \sigma_{1b} + (\sigma_1)_{int} \quad (3)$$

The first coefficient, independent of temperature is equal to $-(4\pi/3)\chi_M$ for a cylindrical sample parallel to the external magnetic field. Those values were calculated from molar magnetic susceptibility values χ_M for the selected gases (CH_4: −12.27 [7], CH_3F: −17.8 [7], CH_2F_2: −24.5 [8], CHF_3: −26.9 [9], CF_4: −31.0 [10], all in ppm ml mol^{-1}), and collected in Table 1.

Since the value of the absolute shielding constant for ^1H of liquid TMS is known and equal to 32.755(24) ppm [11], therefore all the extrapolated results are reported in the absolute nuclei shielding scale according to Eq. (2), i.e. in terms of (σ_o). The experimental data for the parameters of Eqs. (2) and (3) for the fluoromethane/water mixtures are presented in Table 1. For comparison in this table are also reported results of earlier experimental works and of the more recent quantum-mechanical calculations.

The results obtained allowed to determine the mean absolute shielding constants for the ^1H nuclei in isolated H_2O and HDO molecules ($\sigma_o = 30.062$ and 30.101 ppm, respectively). The former result coincides with the generally accepted value of 30.052 ppm [5]; the latter has been reported for the first time. To examine exactly the isotope effects on ^1H nuclear magnetic shifts, it is shown as a plot of its values versus density on Fig. 2. From the quantitative point of view we see that isotope effects are strongly dependent on pressures of the gaseous buffer used.

On this basis the so called secondary isotope effect on chemical shift (IECS) $^2\Delta^1H\ (^{2/1}H) = \delta(^1HDO) - \delta(^1H_2O)$