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Communication

NMR frequency and magnetic dipole moment of ^{3}He nucleus

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ABSTRACT

We present new gas-phase NMR spectra which relate the resonance frequency of ^{3}He nucleus to the resonance frequency of the proton in tetramethylsilane (TMS). We discuss the dependence of ^{3}He resonance frequency on the density of the solvent gas, and we consider in detail the absolute shielding scales of both nuclei. Finally, we analyse the accuracy of the results, using the relationship between the resonance frequencies, absolute shielding constants and magnetic dipole moments of ^{1}H and ^{3}He nuclei.

1. Introduction

An isolated closed-shell helium atom is the simplest chemical system which can be observed in NMR spectroscopy. The most abundant ^{4}He isotope is not magnetically active, but the ^{3}He nucleus with spin $I = 1/2$ is suitable for NMR spectroscopy. The nuclear magnetic dipole moment of ^{3}He has been established in an experiment, relating the observed NMR frequencies of ^{3}He nucleus in the helium atom and ^{1}H nucleus in a liquid water sample [1]. In this work, we present new gas-phase ^{3}He NMR spectra and analyse the ^{3}He resonance frequency as a function of the density of the solvent gas. In this manner, we obtain an estimate of the resonance frequency of ^{3}He nucleus in an isolated atom. The magnetic dipole moment of ^{3}He is determined relating this frequency to the resonance frequency of the proton in tetramethylsilane (TMS)—the commonly used ^{1}H NMR standard.

The determination of the magnetic moment μ_L from an NMR experiment is based on the equation

$$\mu_L = \frac{\nu_L}{\nu_K}\frac{(1-\sigma_K)}{(1-\sigma_L)}\mu_K \tag{1}$$

where σ_K is the shielding constant and ν_K is the NMR resonance frequency for nucleus K in an isotropic sample (with a similar notation for nucleus L). Assuming that all the effects not related to the shielding have been eliminated, one can easily obtain Eq. (1) from

$$h\nu_K = \mu_K(1-\sigma_K)B_z \tag{2}$$

where B_z is the external magnetic field, considering the ratio of NMR frequencies for a pair of different nuclei in the same field. The nuclear magnetic dipole moment μ_K is proportional to the nuclear spin I_K

$$\mu_K = \hbar\gamma_K I_K = \mu_N g_K I_K \tag{3}$$

where μ_N is the nuclear magneton, and γ_K and g_K denote the magnetogyric ratio and the g factor for the bare nucleus, respectively. More precisely, the NMR resonance frequency is related to the maximum projection of the nuclear magnetic moment on the axis of the external field, but when the nuclear spin and the sign of the magnetogyric ratio are known one can obtain μ_K from the NMR experiment.

2. Results

We begin with a brief description of the gas-phase NMR experiment, which required the use of a special probehead. To demonstrate the accuracy of the results, we consider next the ratio of the derived ^{3}He resonance frequency for an isolated He atom with respect to the measured ^{1}H resonance frequency in TMS.

One-dimensional ^{3}He and ^{1}H NMR spectra were acquired on a Varian INOVA 500 FT spectrometer at 300 K. A three-channel probehead operating at 500.61, 381.36 and 76.87 MHz for ^{1}H, ^{3}He and ^{2}H nuclei, respectively, was used. It was a home-adapted Varian variable temperature probehead in which both the original deuterium (lock) channel and VT facilities were left unmodified. For the reconstructed probehead, the duration of the 90° radiofrequency pulse of the ^{3}He channel was 15.5 µs only. The absolute frequencies of NMR signals were determined under the conditions of the lock system tuned to the CD_2 signal of external cyclohexane-d_{12}. The constant frequency of the deuterium lock system allowed us to preserve the same external magnetic field for all measurements. Helium-3: ^{3}He (99.993%, Eurisco-Top, France), sulfur hexafluoride: SF_6 (99.75%, Aldrich) and carbon dioxide: CO_2 (99.8+%, Aldrich)

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from lecture bottles were used for the preparation of the samples without further purification. Gas samples were made by condensing pure gases from the calibrated part of a vacuum line to NMR tubes and sealed, as described in more detail earlier [2]. Helium gas was not condensed when the samples were prepared and it can be estimated that the amount of ^{3}He sealed in our samples varies maximally by ±20%. Density-dependent measurements of the resonance frequency were performed for gaseous solutions of helium-3 in carbon dioxide, CO_2 or sulfur hexafluoride, SF_6, in the gas phase. A small amount of helium-3—approx. 10(2) μg—was used and the resonance frequency was observed at a constant magnetic field (11.76 T) as a function of solvent density (CO_2 or SF_6) in the gas-phase. The outlined approach generally allows for the precise determination of NMR spectral parameters free from intermolecular interactions when the density of solute gas is very small [3]. In case of helium gas the contributions from He...He interactions are practically negligible [4] and do not affect the results of the present experiment. More general information on NMR studies in gaseous solutions can be found for instance in Jameson's early studies of ^{129}Xe [5–7]. We note that, in contrast to ^{3}He NMR, the spectral parameters of ^{129}Xe are extraordinarily sensitive to intermolecular interactions [8].

For low density of helium gas ρ_A, the observed resonance frequency, ν_A, is linearly dependent on ρ_B, the solvent density [2]

$$\nu_A = \nu_{0,A} + \nu_{1,AB}\rho_B \tag{4}$$

where $\nu_{0,A}$ is the frequency extrapolated to the zero-density point. The term $\nu_{1,AA}\rho_A$ is omitted in Eq. (4) because both its constituent parts are negligibly small and consequently this term has no detectable influence on the final results of this study. As shown in Fig. 1, the extrapolation permitted us to determine the ^{3}He resonance frequency free from intermolecular interactions, ν_0. The frequency extrapolated to the zero-density point of gas solvent is $\nu_0(^3\text{He}, 300\text{ K}) = 381.358662(1)$ MHz. At the same magnetic field we have also measured $\nu_H(\text{TMS,liq., } 300\text{ K}) = 500.607621(1)$ MHz using the same NMR probe and all the other experimental features.

At the same time, the results displayed in Fig. 1 give us also the ν_1 parameters, which describe the medium effects in gaseous solutions [9]. The ν_1 values, determined by the slopes of the frequency dependence on the density, in the present experiments are −35(2) Hz L mol^{-1} and −74(1) Hz L mol^{-1} for CO_2 and SF_6, respectively. It appears that these values can be assigned primarily to the bulk susceptibility effects, which are estimated on the basis of available molecular susceptibilities of pure solvents [10] to be −33.2(4) Hz L mol^{-1} in CO_2 and −70.2(4) Hz L mol^{-1} in SF_6 gaseous solvents. We conclude therefore that any contributions from intermolecular interactions to the ν_1 parameters are small in the present results. This is in agreement with the recent theoretical estimates for He-rare gas interactions [4]. Finally, we note that the medium effects contribute only to the ν_1 (or σ_1) parameters and they vanish for the values extrapolated to zero-density (ν_0 and σ_0). Our present analysis of helium-3 nuclear magnetic moment is based exclusively on the latter parameters and therefore it is free from all medium effects.

For the sake of consistency we use $\sigma_H(\text{TMS,liq., } 300\text{ K}) = 32.775(25)$ ppm for the absolute shielding of ^{1}H nuclei, as in our previous investigations [9,11]. The above result is valid for cylindrical tubes parallel to the external magnetic field and serves only for the reading of absolute proton shielding at the investigated point. We have used a single glass tube (2.6 mm i.d. and 4.0 mm o.d.) filled with liquid TMS, degased from atmospheric oxygen and sealed. The absolute shielding of the proton was established from the chemical shift observed between this reference sample and the ^{1}H NMR signal of gaseous methane extrapolated to the zero-density point, $\sigma_H(\text{TMS,liq., } 300\text{ K}) - \sigma_0(\text{CH}_4, 300\text{ K}) = 2.164(1)$ ppm [12]. Following Raynes [13] we have accepted the absolute shielding of protons in an isolated CH_4 molecule equal to 30.611(24) ppm and altogether it gave us the mentioned above $\sigma_H(\text{TMS,liq., } 300\text{ K}) = 32.775(25)$ ppm as the experimental shielding value. Let us add that our recent investigations, based on the shielding measurements of an isolated H_2 molecule and corresponding ab initio calculations [14], give slightly larger (≈0.1 ppm) shielding of protons in liquid TMS [15]. Accounting for the chemical shift of 0.665(1) ppm between pure TMS and 1% TMS in $CDCl_3$ the present shielding result can be easily modified to the value of $\sigma_H(1\%\text{ TMS in CDCl}_3, 300\text{ K}) = 33.440$ ppm, the IUPAC recommended standard for proton chemical shifts [16,17] and it permits the comparison of our measurements of ^{1}H and ^{3}He NMR frequencies with the available data, published by Hoffman and Becker [18]. In our measurements we have obtained $\nu_H = 500.607288$ MHz for this proton reference standard and $\nu_{He} = 381.358662$ MHz for an isolated helium atom; it gives the ν_{He}/ν_H ratio equal to 0.76179207 when all the experimental conditions were preserved exactly the same. Hoffman and Becker measured these frequencies using two different NMR probes and they obtained $\nu_H = 400.1297064$ MHz and $\nu_{He} = 304.8156456$ MHz for two gas-

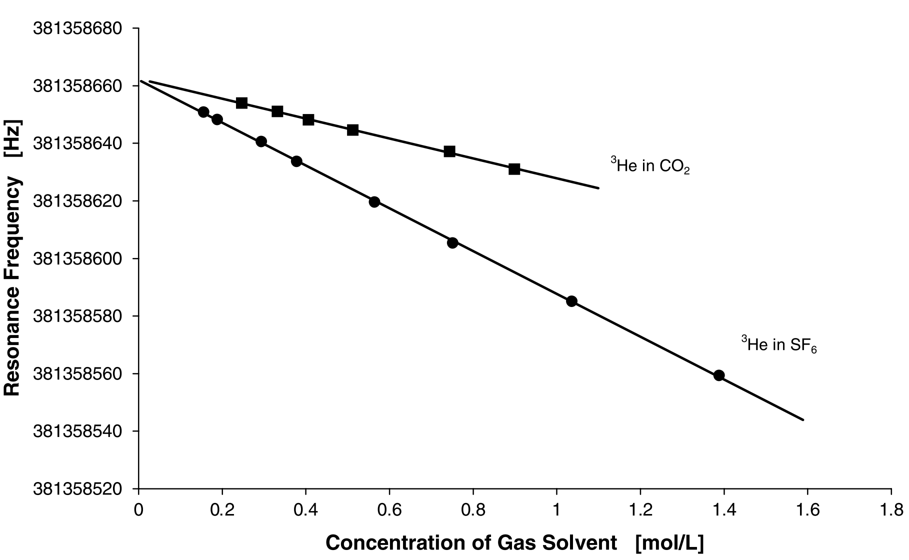

Fig. 1. Density-dependent ^{3}He NMR frequency at a constant external magnetic field (11.76 T).

eous samples of helium-3 at 301 K [18], which yields $\nu_{He}/\nu_H = 0.76179209$. The agreement is excellent and cannot be accidental, although Hoffman and Becker used the CD_3 signal of methanol-d_4 as the deuterium lock [18], while our present measurements were performed with the CD_2 signal of cyclohexane-d_{12} as the deuterium reference. It did not make any difference as each complete set of measurements, that described in Ref. [18] and our own, was performed with a consistent use of the same lock.

3. Discussion

As a first test of the accuracy of our results, we use Eq. (1) to derive the value of the magnetic dipole moment of ^{3}He. The absolute shielding constant in the He atom, proportional to the expectation value $\langle 1/r \rangle$ (r is the electron–nucleus distance), is $\approx$59.9367794 ppm [19]. For hydrogen, we use σ_H(TMS,liq., 300 K) = 32.775 ppm and the best presently available value of ^{1}H magnetic moment, $\mu_H = 2.792847337\ \mu_N$ [20]. Finally, for the frequency ratio ν_L/ν_K needed in Eq. (1) we obtain from our measurements 381.358662/500.607621 = 0.7617915629. The magnetic moment of ^{3}He determined from these data is $-2.12762532977\ \mu_N$. The value of the ^{3}He magnetic dipole moment based on the literature data is $-2.12762523466\ \mu_N$ [1,21]. We consider the agreement of these two results as very satisfying—in our experiment, the shielding and resonance frequency of the ^{1}H nucleus refer to a different molecule (TMS vs water in Ref. [1]), and nevertheless the derived magnetic moment is $\approx$1.000000045 of the quoted value.

To analyse the error bars of our result, we need to consider only the errors in both shielding constants; the ratio of the NMR resonance frequencies and the magnetic moment of ^{1}H are much more precise. For He, there are estimates of the neglected effects, such as the relativistic correction, ±0.04 ppm [22] and the correction for finite ^{3}He nuclear mass, approximately $-.01$ ppm [23]. They indicate that the error in the He shielding most likely does not exceed 0.05 ppm. The absolute shielding of ^{1}H can be estimated independently using the value of the shielding in H_2 and the measured chemical shift, $\sigma_H(\text{TMS,liq., } 300\text{ K}) - \sigma_0(H_2, 300\text{ K})$. For H_2, the value deduced from experimental spin-rotation constant and calculated diamagnetic shielding contribution is $\sigma_0(H_2, 300\text{ K}) = 26.288(2)$ ppm [14]. This result, combined with the chemical shift, indicates that the shielding σ_H (TMS,liq., 300 K) may be $\approx$0.1 ppm larger than the literature value we have used. Although most likely the accuracy of the H_2-based estimate is higher, we shall use the literature value and 0.2 ppm as the error bar for σ_H(TMS,liq., 300 K). We find that with the changes of the proton and helium shielding constants used as input data the derived magnetic moment of ^{3}He varies between 0.999999795 and 1.000000295 of the literature value. These changes are too small to draw definite conclusions about the accuracy of the shielding constants.

To check the consistency of the results we can also rewrite Eq. (1) as

$$\sigma_K = 1 - \frac{\nu_K}{\nu_L}\frac{\mu_L}{\mu_K}(1 - \sigma_L) \tag{5}$$

In this context, we assume that the frequencies and the magnetic moments are known. The advantage of Eq. (5) is that the derived value of σ_K depends very strongly on the accuracy of the resonance frequencies and magnetic dipole moments used as input data. This equation can be applied to analyse the shielding constants for any pair of nuclei in any molecules; we have used it successfully to examine the magnetic dipole moments for a series of nuclei [9,11]. In this work, we compute the shielding σ_{He} for different values of σ_H, ν_H and ν_{He} (to simplify the analysis, with the literature value of μ_{He}). Using $\sigma_H = 32.775$ ppm and the measured frequency ratio, 0.76179156, we obtain from Eq. (5) $\sigma_{He} = 59.892$ ppm, in good agreement with the correct value. On the other hand, if we use for the frequency ratio a slightly different value, 0.76179437 [16] and the corresponding $\sigma_H = 33.440$ ppm, we derive $\sigma_{He} = 56.872$ ppm, indicating an inconsistency of these input data (in the recent 2008 IUPAC recommendations [17], the discussed above frequency ratio, 0.76179437, was corrected according to the results of Hoffman and Becker [18]).

4. Conclusions

The 2001 IUPAC recommendations [16] already suggested the desirability of using gaseous helium-3 as a universal standard of chemical shifts but found it rather unpractical. With the accurate value of ^{3}He shielding and the present measurements of the ^{3}He resonance frequency free from all the medium effects we are a step closer to the use of $\sigma_{0,He}$ as the universal standard of nuclear magnetic shielding. Applying Eq. (5) it is possible to determine the shielding constants of other nuclei in molecules whenever the nuclear magnetic moments are known with sufficient accuracy. In principle, only a few technical problems still justify the necessity of measuring the chemical shifts with respect to specific reference standards for these nuclei. Thus, one can imagine that the future NMR spectrometers will be able to convert routinely the frequencies measured for arbitrary nuclei to the scale of nuclear magnetic shielding.

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