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Probing Nuclear Dipole Moments and Magnetic Shielding Constants Through 3-Helium NMR Spectroscopy

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Abstract: Multinuclear NMR studies of the gaseous mixtures that involve volatile compounds and ³He atoms are featured in this review. Precise analyses of the ³He and other nuclei resonance frequencies show linear dependences on the gas density. Extrapolation of the gas phase results to the zero-pressure limit gives vo(³He) and vo(ⁿX) resonance frequencies of nuclei in a single 3-helium atom and nuclei in molecules at a given temperature. The NMR frequency comparison method provides an approach for determining different nuclear magnetic moments. Application of quantum chemical shielding calculations which include a more complete and careful theoretical treatment allows the shielding of isolated molecules to be achieved with great accuracy and precision. They are used for evaluation of nuclear moments without shielding impact on bare nuclei: ^{10/11}B, ¹³C, ¹⁴N, ¹⁷O, ¹⁹F, ²¹Ne, ²⁹Si, ³¹P, ³³S, ^{35/37}Cl, ³³S, ⁸³Kr, ^{129/131}Xe, and ¹⁸³W. On the other hand, new results of nuclear moments were used for reevaluation of absolute nuclear magnetic shielding in molecules under study. Additionally, ³He gas in water solutions of lithium and sodium salts was used for measurements of ^{6/7}Li and ²³Na magnetic moments and reevaluation of shielding parameters of Li⁺ and Na⁺ water solvated cations. In this paper, guest ³He atoms that play a role in probing the electron density in many host macromolecules are presented as well.

Keywords: nuclear magnetic dipole moment; nuclear magnetic shielding; gas-phase NMR

1. Introduction

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Helium (He) is a chemical element with atomic number 2 located by IUPAC in group 18 (or 8A) of the Periodic Table of Elements [1]. It is a colourless, odourless, tasteless, inert, monoatomic gas. Helium is the second most abundant element in the universe. However, in the Earth's atmosphere and in natural gas, it is only 5.2 ppm by volume. Seven times lighter than air, it is able to escape from the Earth's atmosphere to space. Radiogenic helium in natural gas fields occurs in concentrations up to ~7% by volume and can be extracted commercially by a low-temperature fractionated distillation process. For the NMR community, the use of liquid helium as cooling material for superconducting electromagnets in spectrometers is well known. Two stable helium nuclei are known: ³He and ⁴He.

Both of them play an important role in cryogenics [2]. ⁴He can be a liquid at low temperature 4.22K (-268.93°C) and can be a solid at a pressure of 25 atm and temperature of 0.95K (-272.2°C). Liquid ³He can be used as a refrigerant in the separated phase solution of ³He in ⁴He where a temperature below 0.1K is reached. In these very low temperatures it shows characteristic superfluid properties (Helium II) [3]. The natural abundance of ³He is of the order of 0.000134%, but only this isotope with spin number I=1/2 can be used in NMR and MRI measurements. The use of artificially enriched material is then obligatory. Most of the rare isotope of helium is produced from the decay of tritium during the maintenance of nuclear weapons in the United States and then accumulated in a stockpile. Tritium (T, ³H) is the radio-active isotope of hydrogen with a half-life of 12.32 years.

The ³He nucleus - also known as helion (³He⁺², symbol h) – is composed of 2 protons and one neutron is magnetically active. Two simple requirements are obligatory for successful measurements in the NMR spectrometer. It is necessary to have a suitable transmitter with an available helium frequency and probe with adequate generated resonance tuned to the helium frequency [4]. Actually, many NMR spectrometers do not meet these conditions. Nevertheless, some practical measurements were performed in this field in gaseous, liquid and solid states. If samples are enriched in the helium-3 isotope the sensitivity of NMR analysis is high enough. The resonance signals are sharp when appearing at spectral range extending from 10 up to -50 ppm. Since helium does not form any "normal" covalent compounds the NMR experiments have a physical rather than chemical character. In recent years, an experiment with helium-3 revealed a very valuable method of investigation for the specific intermolecular-interactions in the gas phase *e.g.*[5]. Helium atoms are completely chemically inert and do not form any stable compounds. Interestingly, helium-3 atoms can be

included into fullerenes and nanotubes and used as probes of a magnetic shielding molecular interior. This aspect of NMR investigations will be discussed at the end of our review. Novel developments of ³He NMR are connected with nuclear hyperpolarisation techniques, carried out in different ways, to receive signals even 10000 times greater per atom than those produced routinely at thermal equilibrium [6]. A new, general method of NMR spectra measurements expressed in shielding scales, known as the "Alternative Approach to the Standardization of NMR Spectra", was proposed using the ³He NMR resonance reference [7]. For this purpose, the ³He NMR spectra were measured simultaneously with residual proton and carbon signals of different deuterated solvents when helium-3 was dissolved. The experimental shielding of deuterated solvents determined in this way are characterised with high accuracy and precision. They will be used in the next steps of this work. The main part of this review is devoted to the NMR method of NMM measurements. The role of ³He NMR spectroscopy in establishing nuclear magnetic moments and magnetic shielding constants is discussed in detail. We utilised the ³He (helium) atom used in mixtures with simple molecules that possessed the nuclei of interest, *e.g.*: ³¹PH₃, ¹³CH₄, ¹⁴NH₃, ¹¹BF₃, ²⁹SiH₄, H³⁷Cl and some others. Additionally, a few comments on helium-3 NMR achievements and prospects are also included. The Scheme(1) of nuclei studied by NMR spectroscopy and shown below:



Scheme 1. A set of nuclei which were studied by NMR spectroscopy using ³He as a reference for measuring its nuclear magnetic moments.

2. Methodology of measurements of nuclear magnetic moments

2.1. Methodology of gas phase NMR experiments

Many physical properties of gases can be conveniently characterised in terms of general virial theorem. In this case the nuclear magnetic shielding dependence of any nucleus in pure gas molecule $\sigma(Q,T)$ can be described as virial expansion in the density function (Q) at a given temperature (T) [8]: $\sigma(Q,T) = \sigma_0 + \sigma_1(T)Q + \sigma_2(T)Q^2 + \sigma_3(T)Q^3 + ...$ (1)

where σ_0 is the shielding constant of the nucleus in the "isolated" atom or molecule and σ_1 , σ_2 , σ_3 are virial coefficients resulting from many body collisions. Below ~ 40 atm (density 1.64 mol/L at 297K) the dependences are strictly linear because only the first two coefficients are present:

$$\sigma(\varrho, T) = \sigma_0 + \sigma_1(T)\varrho \tag{2}$$

Analogous equations can be treated when the mixtures of gaseous substances are investigated. These systems can be considered as the binary mixtures of gaseous substance A containing the nucleus X whose shielding $\sigma(X)$ is measured, and gas B is the solvent. Equation (1) can be formulated as: $\sigma(X) = \sigma_0(X) + \sigma_{AA}(X)QA + \sigma_{AB}(X)QB + ...$ (3) Nuclear magnetic shielding constants can be measured also in liquid solutions of different substances. Here, water solutions of inorganic salts are of most importance. So, several water salt solutions were investigated to establish the nuclear magnetic moments of inorganic isotopes. The analysis of chemical shifts measured in some mixtures of different concentrations is much more complicated than that of gases because of nonlinearity dependences. In this case, polynomial functions are more useful: (5)

$$\sigma(X) = \sigma_0(X) + \sigma_{AB}(X)QB + \sigma_{AB}(X)QB^2$$

where $\sigma_0(X)$ means the isotope in solvated cation or anion under study. The final equation forms (2), (4) and (5) will be exercised for numerous individual cases in details in the next sections.

2.2. Nuclear magnetic dipole moments and shielding constants

The main field of the induction resonance technique was to determine the dipole moment of a given nuclei. For atomic nuclei, the intrinsic angular momentum of particle (p) is directly proportional to its magnetic moment (μ): μ = γ p, where the proportionality constant γ is the magnetogyric ratio. The dipole magnetic moment is a vector, but only the projection value that is partially in the direction of the magnetic field can be measured in experimental conditions. The nuclear magnetic moment (NMM) μx is related to the nuclear spin number as:

$$\mu x = \hbar \gamma x I x = g x I x \mu N \tag{6}$$

where γx is the nuclear gyromagnetic ratio, $\mu N = 5.050783699(31) \times 10^{-24}$ J/T is the nuclear magneton and gx is the g factor of nucleus X. The first measurements of NMM were performed by I.I.Rabi [9] who has predicted that magnetic moments can flip their magnetic orientation in field B₀ when they have been forced to absorb tiny parts of energy from additional electromagnetic field B₁. These transitions can be detected when spins go to the lower energy orientations. He called this method atomic or molecular beam magnetic resonance (ABMR). This approach was a prototype of the well-known spectroscopic method NMR (Nuclear Magnetic Resonance) carried out in a static magnetic field in bulk macroscopic samples. The NMM precess (rotate) in the magnetic field around the z axis at a constant rate ω_L which can be observed in the NMR spectrometer as a radio resonance frequency (rf). The equations that determine the resonance frequencies of two different nuclei, vx and vy, in the resonance condition are as follows:

$$hvx = (1 - \sigma x)B_z \tag{7}$$

$$hv_{\rm Y} = (1 - \sigma_{\rm Y})B_{\rm z} \tag{8}$$

where σ_x and σ_y are the absolute shielding constants. In reality the shielding (screening) effects in the matter can slightly change the Larmor frequency of any given nuclei in the molecule, depending on the chemical environment of the nucleus within a molecule. It is difficult to measure the strength of the magnetic field with high precision. This problem can be avoided if the ratio of frequencies in eq.(7) and (8) is measured. Dividing both equations, it is possible to eliminate the external magnetic field induction B₀ and receive the very useful relation:

$$\Delta \mu_{\rm X}^{\rm z} = \frac{\nu_{\rm X}}{\nu_{\rm Y}} \cdot \frac{(1 - \sigma_{\rm Y})}{(1 - \sigma_{\rm X})} \cdot \Delta \mu_{\rm Y}^{\rm z} \tag{9}$$

often used for evaluation of unknown NMM from other taken as references. The nuclear dipole moment of the reference nucleus should be known with the best possible precision and accuracy. Proper measurements of nuclear magnetic moments require corrections for shielding constants (σ) of the given and reference nucleus f=(1- σ Y)/(1- σ X). These correction factors (f) are usually more or less different than 1.00, which means that shielding effects in atoms and molecules change the proper nuclear magnetic moments. New and now more accessible, sophisticated theoretical calculations of shielding parameters have provided a new impetus for remeasuring moments with great accuracy and

3

The most

precision.

excellent result for the nuclear dipole moment was established very recently for proton $\mu({}^{1}H)=\mu_{P}$. The new physical method for direct high-precision measurement of a single isolated proton in a double Penning trap gives the value $\mu_{P}/\mu_{N} = g/2 = 2.79284734462(82)\mu_{N}$ [10]. The magnetic moment is here expressed in units of nuclear magnetons. The most fruitful method for establishing heavier magnetic dipole moments of stable nuclei is NMR spectroscopy, since resonance techniques are able to give fixed values very precisely and accurately. Locating a macroscopic sample in a uniform stable magnetic field, it is possible to measure Larmor frequencies coming from different nuclei present in a sample. These nuclei can originate from the same molecule or different molecules that are simply present in the sample under study. This approach allows the assignment of appropriate frequency relations and, as a consequence, the comparison of two or more NMMs. The basis for further calculations is a good knowledge of one NMM from the pair of chosen nuclei. One can usually use ${}^{1}H$ (proton) as a reference. Other referenced nuclei can be deuteron D(${}^{2}H$), helion ${}^{3}He$ or fluorine ${}^{19}F$. In this paper, the second example was mostly used. The other form of Equation (9) can be used to check the consistency of nuclear magnetic moments and shielding factors:

$$\sigma_{\rm X} = 1 - \frac{v_{\rm X}}{v_{\rm Y}} \cdot \frac{\Delta \mu_{\rm Y}^{\rm z}}{\Delta \mu_{\rm X}^{\rm z}} \cdot (1 - \sigma_{\rm Y}) \tag{10}$$

All parameters used in this formula are the same as stated above. It is very convenient to exercise Equation (10) when complex molecules are studied and data for additional nuclei can be applied.

3. Results and Discussion

3.1. ³He chemical properties

The helium atom and hellion nucleus can be categorised as unusual physical objects. A very small atomic diameter (28 pm, 1pm=10⁻¹²m) can cause the glass walls to be penetrated and the glass ampoule to be emptied. This is an indication for fast experimental maintenance of samples containing helium-3 atoms. It is remarkable that the ³He nucleus is the only stable nucleus with a proton number larger than neutrons. The mirror nucleus of helium-3 is the tritium nucleus with 2 neutrons and one proton (T=3H). The sign of the ³He nuclear magnetic moment is opposite to that of proton [11], negative by convention. Precise knowledge of the helium-3 NMM as a reference is crucial for employing the NMR method for establishing nuclear dipole moments against that of hellion. Several attempts have been made to precisely determine the ³He nuclear magnetic moment. All were undertaking using NMR spectroscopy. The ³He magnetic moment was measured by Anderson & Novick [12], Williams & Hughes (1968 [13]), Neronov & Barzakh (1977 [14]), Belyi & Shifrin (1986 [15]), Hoffman & Becker (2005 [16]), Jackowski et al.(2008 [4]), Aruev & Neronov (2012 [17]) and Makulski (2020 [18]). In our opinion, the best result was achieved by Flowers, Petley and Richards [19] in pure helium-3 samples against the proton signal in liquid water. The authors have measured the ratio of the NMR spin precession frequencies of optically pumped low pressure helium-3 and proton in water, taking into account residual inhomogenities and water diamagnetic corrections accurately. The final results of the nuclear magnetic moment μ (³He)=-2.127625308(25) μ N were corrected by factors that arose from shielding parameters of helium-3 $\sigma_0(^{3}\text{He})=59.96743(10) \text{ ppm [20]}$. It was included in the latest collections of fundamental physics constants recommended by Stone in the "Table of recommended nuclear magnetic dipole moments" published under the auspices of the INDC (International Nuclear Data Committee), November 2019 [21]. This value was used for all recalculations of nuclear moments of different nuclei carried out previously and mentioned in this work. It is worth to remember that the nuclear moments are rather experimental than theoretical values. The nuclear moments can be calculated purely theoretically using several nuclear models. Last calculations lead to essentially different results: -1.913042µN (shell model), -2.2905µN (QCD model) and -2.004914µN (Quark model), where QCD means lattice quantum chromodynamics theory[22]. The difference to the best experimental value is rather large (~5% in the last case) and confirms the assumption of nuclear moments significance as experimental values. From the quantum mechanical point of view, the ³He nucleus is fermion, while ⁴He nucleus is a boson. Several chemical properties of the helium atom and helion nucleus are shown in Table 1. The NMM μ (³He) and spin number (1/2) decide on the radiofrequency used for detection of this nuclei in the stable magnetic field. Ξ frequency parameter is defined as the ratio of 3-helium frequency v₀(observed) to that for ¹H of TMS in CDCl₃ in the same magnetic field, expressed as a percentage. For example, in magnetic field B₀=11.74 T, ³He radiofrequency is 381.3575 MHz, just between frequencies for ¹⁹F (470.910 MHz) and ³¹P (202.595 MHz). In this way, the Ξ /MHz is 76.178972 [23]. Fortunately, these measurements are available on Varian INOVA (now Agilent) spectrometers. Relaxation times of ³He nuclei in the pure gas phase are very long, up to several thousand of seconds. Therefore, the usage of short pulse duration and long relaxation delays are strongly recommended. The linewith of recorded signals often do not exceed 1 Hz.

Property		Property	
Spin	1/2	Natural abundances	0.000137%
Magnetic moment	-2.127625308	Isotope mass	3.0160293 u
Chemical shift range	58 ppm	Half life	stable
Frequency ratio	76.18%	Boiling point	3.19K
Reference compound	³ He gas	Critical point	3.35 K
Linewidth of reference	0.3 Hz	Heat of vaporization	0.026 kJ/mol
T1 of reference	1000 s	Melting point	below 1mK
Receptivity rel.to ¹ H	0.442 when enriched	Covalent radius	32 pm
Magnetic susceptibility	-1.88 cm ³ /mol	Van der Waals radius	143 pm

Table 1. Physical and magnetic properties of ³He atoms and nuclei.

3.2. Other noble gases: ²¹Ne, ⁸³Kr, ^{129/131}Xe

A simpler and effective example for handling Equations (2) and (4) for establishing the nuclear magnetic moments is provided by mixtures of noble gas isotopes that possess the non-zero spin numbers. The mixtures of ³He as reference nucleus with other noble gas atoms were carried out using the NMR method: ²¹Ne [24], ⁸³Kr [25], ¹²⁹Xr and ¹³¹Xe [26]. The frequency dependences as functions on the density of the main gaseous ingredients are shown in Figure 1.

The appropriate input data for nuclear magnetic moment calculations - frequency ratios, correction factors and final nuclear magnetic moments data are shown in Table 2. Thanks to the high receptivity of ³He NMR signals the precise evaluation of magnetic moments is mainly a function of shielding correction factors. The correction factor for ²¹Ne is small ~0.05% but very valuable for xenon isotopes 0.7%. The results marked with asterisks, were calculated against the deuterium ²H(D) resonance used in the lock system. It can be seen that both kinds of results for helium, krypton and xenon are in very good agreement. This circumstance justifies using the lock system instead of 3-helium for measuring the ²¹Ne nuclear moment.



Figure 1. NMR frequency dependences on the density of gaseous noble gases: ³He (in Xe), ²¹Ne, ⁸³Kr, ¹²⁹Xe and ¹³¹Xe, in magnetic field B₀=11.7574T.

In our spectrometer, low frequency resonances (like ²¹Ne and ⁸³Kr) should be measured in a broad band probe with test tubes that have a 10 mm external diameter, whereas high frequencies (like ³He) are only available in a special probe with NMR tubes that have a 5 mm external diameter [4].

Table 2. NMR parameters for calculating $\mu(^nX)$ nuclear magnetic moments of noble gases. *Nuclear Magnetic Moments from ²H(D) parameters.

System	$v_0(^nX)/v_0(^3He)$	Correction factor	μ(ⁿ X)	References
³ He	1.0000	1.000059965	-2.127625308(10)	[19,20]
			-2.127625307(10)*	[25,26]
²¹ Ne/ ³ He	0.103638	1.000497422	0.66184(7)	[27]
			0.6617774(10)*	[24]
⁸³ Kr/ ³ He	0.0505161561(5)	1.003529996	-0.97072965(32)	[25]
			-0.97072965(32)*	
¹²⁹ Xe/ ³ He	0.36309748(3)	1.007022726	-0.777961(16)	[26]
			-0.777961(16)*	
¹³¹ Xe/ ³ He	0.107634919	1.007022726	0.691845(7)	[26]
			0.691845(7)*	

From the final results of NMMs measured against ³He and ²H(D) nuclei (Table 2), it is clear that both are very congruent and can be used interchangeably in these experiments. The accuracy is strictly connected with shielding

factors which are large for heavy nuclei and small for light nuclei. Shielding parameters of the lock system (2H,D), for these purposes, show very good quality [4].

3.3. Simple hydrides: ¹³CH₄, ¹⁴NH₃, H₂¹⁷O, ²⁹SiH₄, ³¹PH₃, H^{35/37}Cl

Actually, the investigations of simple, gaseous hydrides are optimal for accurate results of shielding and magnetic moments of nuclei. The range of ¹H NMR shifts is very small, practically limited to ~10 ppm and experimental errors are much less than 0.1 ppm. The shielding constants are very well known from experimental [28] and theoretical [29] studies. Binary hydrides CH₄, NH₃, SiH₄, PH₃ and HCl are gases at normal conditions and can be used directly from lecture bottles for preparation of gaseous samples for NMR measurements. Furthermore, the isotopically enriched substances (*e.g.* ¹³CH₄, ¹⁵NH₃) are ofered from commercial sources. They were formerly used in our systematic investigations [30-34]. More problematic were the attempts to prepare water containing gaseous samples; firstly a 25% enriched preparation was used [35] and next, even 90% H₂¹⁷O [36]. In this last case, the samples containing ~5×10⁴ mol/L enriched water in buffer gases CH₃F, CHF₃ were made and the ¹⁷O spectra were measured with success. All suitable input data for calculations of nuclear magnetic moments are shown below in Table 3.

Table 3. NMR parameters in simple hydrides for calculation of nuclear magnetic moments of ¹³C, ¹⁴N, ¹⁷O, ²⁹Si, ³¹P and ^{35/37}Cl nuclei from gas phase experiments. (*) means values calculated from ¹H NMR data.

System	$v_0(nX)/v_0(^{3}He)$	Correction factor	μ(ⁿ X)	References
¹³ CH ₄ / ³ He	0.330074361(2)	1.00013507	0.70236944(68)	[30]
			0.70236945(68)*	
¹⁴ NH ₃ / ³ He	0.094821748(5)	1.00020688	0.40357377(45)	[31]
			0.40357367(40)*	
H ₂ ¹⁷ O/ ³ He	0.177949095(15)	1.00026852	1.893553(3)	[36]
			1.893553(2)*	[35]
²⁹ SiH4/ ³ He	0.260768297(3)	1.00042308	-0.5550520(3)	
			-0.5550520(3)*	[32]
³¹ PH ₃ / ³ He	0.531248246	1.000555132	1.1309247(50)	[33]
			1.1309246(50)*	
H ³⁵ Cl/ ³ He	0.12862043	1.000917130	0.821716(5)	[34]
			0.821721(4)*	
H ³⁷ Cl/ ³ He	0.07063037	1.000917130	-0.683997(5)	
			-0.683997(4)*	

3.4. Fluoride compounds: ^{10/11}BF₃, ³³SF₆, ¹⁸³WF₆

Unfortunately, not all elements form simple hydrides which are regular gases or volatile liquids at room temperatures. In such cases, one can use the fluorinated analogs of hydrides which often are available as commercial chemicals. The benefit of using ¹⁹F nuclei is their high sensitivity, almost equal to that of proton and the universal

ability of measurements in most spectrometers. In the case of boron, it is suitable for analysing trifluoroborane BF₃ gas rather than diborane B₂H₆ - with a specific structure composed of two bridge H atoms between boron atoms and four H terminal atoms. In the end, we used BF₃, which has a trigonal planar structure with D_{3h} symmetry [**37**]. Its vapour pressure at 20°C is more than 50 atm and it can be investigated in a large density range. Analogically, similar experiments were performed with sulfur hexafluoride SF₆ gas in the 5 -25 atm pressure range [**38**]. A big advantage of using this compound is its high octahedral symmetry consisting of six fluorine atoms connected to one central sulfur atom. The electric field gradient (EFG) on sulfur nuclei is then zero and ³³S signals are very narrow ~1 Hz. Other gaseous sulfur containing compounds: H₂S, COS, SO₃ and SO₂ are notable for much worse NMR measurement conditions. The gaseous samples containing small amounts of 3-helium atoms dispersed in sulfur hexafluoride were used. Well resolved sulfur-33 NMR spectra gave the opportunity to recognise the ¹J(³³S, ¹⁹F) spin-spin coupling and make use of the INEPT (Insensitive Enhanced Polarisation Transfer) sequence to amplify the signal and to smooth the base line in the spectrum. For example, the ³³S NMR INEPT spectrum of 21.8 atm (0.89 mol/L) SF₆ is shown in Figure 2: A) coupled to six fluorine-19 nuclei, and B) fully decoupled.



Figure 2. The ³³S NMR spectra of gaseous SF₆ at 21.8 atm: A) coupled to six fluorine nuclei and B) fluorine-decoupled.

The linear density dependences of ³He and ³³S radiofrequencies were shown in Figure 3. The observed Larmor frequencies, extrapolated to the zero pressure limit, belong to the isolated SF₆ molecule and helium atom. Application of Eq.(9) gives the ³³S nuclear magnetic moment in terms of that of ³He μ (³³S)=0.6432555(10) μ N. The new result is in good agreement with previously reported values μ (³³S)=0.6432474(107) μ N [**39**] and μ (³³S)=0.643251(16) μ N [**40**], but more accurate by one order of magnitude. The shielding corrections for sulfur nuclei σ (³³S)=392.6 ppm in SF₆ were taken from the first relativistic calculations performed previously [**41**]. This value, recalculated from Equation (10) using fluorine parameters – frequency and shielding constantis – 406.2 ppm is in moderate agreement with the calculated one.



Figure 3. ³He and ³³S NMR frequencies as density function of gaseous mixture ³He-SF₆.

Another important modification of the procedure shown above relies on measurements of ¹⁸³WF₆ substance where CF₄ or C₂F₆ gaseous buffers were used [**42**]. They are necessary for lengthening the relaxation times and narrowing the ¹⁸³W resonance signals. Naturally occuring tungsten (wolfram) contains only one isotope (¹⁸³W) with a non-zero value of I=1/2 and natural abundance of 14.31% with rather poor receptivity of 1.06×10^{-5} relative to ¹H. This is where it gets weird. ¹⁸³W is α -particle emitter with a long half-life >1×10¹⁷ y. The ¹⁸³W NMR spectra were recorded using the INEPT (insensitive nuclei enhanced by polarisation transfer) sequence for increasing the signal-to-noise ratio and for smoothing the base line distortions. They were decoupled from ¹⁹F nuclei during acquisition making use of the known spin-spin coupling ¹J(F,W)=43.75 Hz. The isotope effect observed in ¹⁹F NMR spectra connected with substitution of ¹⁸³W by other tungsten isotopes is negligible. The ¹⁸³W nuclear magnetic moment obtained in this experiment was $\mu(^{183}W)=0.116953(18) \mu_N$ which gives the g-factor g₁= $\mu(^{183}W)/I=0.233901(18)$ and gyromagnetic ratio γ_1 =g₁ μ_N/h =1.120249×10⁷ rad s⁻¹ T⁻¹. The experimental results were corrected by the shielding constant of tungsten in WF₆ calculated theoretically $\sigma(^{183}W)$ = 6221.0 ppm [**4**1]. The appropriate NMR parameters for ³He/fluoride compound systems were collected in Table **4**.

System	$v_0(^nX)/v_0(^3He)$	Correction factor	μ(ⁿ X)μ _N	Reference
¹⁰ BF ₃ / ³ He	0.141033238	1.000037916	1.8004636(8)	[37]
			1.80045428*	
¹¹ BF ₃ / ³ He	0.421170045	1.000037916	2.6883781(11)	
			2.6883642*	
³³ SF ₆ / ³ He	0.100744802	1.0003926	0.6432555(10)	[38]
			0.6432467(16)*	
¹⁸³ WF6/ ³ He	0.054630264	1.0061996	0.116953(18)	[42]
		1.0062286	0.116953*	
		1.0061989	0.116950**	

Table 4. NMR parameters for calculations of ^{10/11}B, ³³S and ¹⁸³W nuclear magnetic moments against that of ³He. *NMM measured from ¹⁹F parameters. ** NMM measred from ¹⁹F parameters with theoretical shielding correction factor.

It is obvious that the ¹⁹F nuclear magnetic moment can be calculated from the helium-3 results used in the above mentioned cases: BF₃/³He, SF₆/³He and WF₆/³He systems. If we utilise the measured ¹⁹F frequencies and shielding results that come from the best relativistic calculations, the new ¹⁹F NMM values are as follows:

 $\mu(^{19}\text{F})=2.6283348(26)\mu_N$, $\mu(^{19}\text{F})=2.6283711(132)\mu_N$ and $\mu(^{19}\text{F})=2.6283925(263)\mu_N$, respectively. They are in adequate agreement with those used in previously published results: $\mu(^{19}\text{F})=2.628321(4)\mu_N$ [21] and $\mu(^{19}\text{F})=2.628335(11)\mu_N$ [40] but in disagreement with the result given previously in literature tables $\mu(^{19}\text{F})=2.6288868(8)\mu_N$ [40]. The deviations mainly arise from the shielding uncertainties of fluorine nuclei. It is important to mention the special position of hydrogen fluoride (HF) in fluorine NMR spectroscopy. This simple molecule has one undesirable feature – it forms very corrosive and penetrating fumes with traces of water when hydrofluoric acid is forming. It attacks the glass vessels and vacuum lines mostly used in laboratories for sample preparation and handling. The intermolecular hydrogen bondings in HF are very strong and obtaining monomers, even in the gaseous phase, is very problematic. Nevertheless, the HF molecule was the basic molecule for establishing the ¹⁹F NMR absolute shielding scale [43]. The special conditions were ensured: a thin-walled cell from polyethylenes and Monel metal vacuum line for the transfer of HF and other gases. The results of this investigation have never been repeated and confirmed. For this reason the secondary reference substances were usually used: SiF4 and CFCl₃ [44].

In light of these considerations and taking into account the remarks on the fluorine shielding scale, it is strongly recommended to reevaluate this absolute scale in new experimental and theoretical studies.

3.5 Water solutions: 6/7Li and 23Na salts

Helium-3 can certainly be used as a reference in NMR measurements of nuclei when the water solutions of different cations are the target of the studies. Neither the lithium nor the sodium elements form any stable gaseous compounds. Li-He, the very weekly interacting Van der Waals chemical compound, is probably only present in low temperatures [45]. The most studied objects in lithium and sodium chemistry are their water solutions and they were used in NMM measurements. 1.5 mg of the helium atoms can be dissolved in pure water at 20°C and 1 bar pressure. Additionally, the shielding correction factors can be known from theoretical studies of Antušek *et al.* [46]. These results make use of our new experimental reports on NMR frequencies of Li⁺ [47] and Na⁺ [48] in water solutions of different salts. The concentration dependences do not show linear functions but can be fitted with a quadratic one. In these cases,

the frequency results do not belong to a simple isolated cation but rather to a few aquatic structures of central ions occurring in different mole fractions. In the case of lithium cation - because of its small radius 90pm - as Li(H₂O)₄⁺ cation, the shielding correction is 91.69 ppm in the infinitely diluted solution. In the octahedral coordinating lithium cation this value is 90.89 ppm. Both results can give the ⁶⁷Li nuclear magnetic moments as the lower and upper limit of these numbers. In the case of the ²³Na magnetic moment the situation is much more complicated. Sodium cation Na⁺ is dynamically transformed between several structures according to the equation:

 $Na(H_2O)_{3^+} + H_2O \leftrightarrow Na(H_2O)_{4^+} + H_2O \leftrightarrow Na(H_2O)_{5^+} + H_2O \leftrightarrow Na(H_2O)_{6^+} + H_2O \leftrightarrow Na(H_2O)_{7^+}$ (11)

The molecular dynamics (MD) simulation results suggest that the five coordinated sodium ion is the most populated structure (~60%) and the six-coordinated structure is the second most (~30%) [49]. In this case, we prefer to consider the dynamic character of water surrounding the central cation by averaging the results for 4, 5 and 6-coordination systems with their appropriate molar fractions. 580.12±10 ppm for the shielding correction factor of sodium cations in liquid water was finally received.

The helium-3 correction factor in lithium water solutions was measured as 2.7675(25) ppm and 2.747(2) for sodium salts against that of the isolated ³He atom in the gas phase in the chemical shift category. Taking into account the volume magnetic shielding susceptibility effect of pure water ($4/3\chi v$, where χv is volume susceptibility), the shielding corrections are of the order of 0.24 ppm compared with the gas phase in the relative shielding scale. For ^{6/7}Li and ²³Na nuclear magnetic moments, the NMR results are very consistent with ABMR results achieved previously [50] where shielding corrections are made for atomic inert species which are: $\sigma(Li)=147.2$ ppm and $\sigma(Na)=640.62$ ppm. NMMs of lithium and sodium nuclei measured using the NMR and ABMR methods are shown in Table 5. Additionally, new results published by Neronov [51,52] were also included. They were achieved using an interesting method of simultaneous observation of the two spin system with an adapted NMR spectrometer, which reduced the random and systematic errors and by an order of magnitude.

System	ν(6Li)/ν(3He)	correction factor	μ(^e Li)	Reference
Li ⁺ water solution/ ³ He	0.193177745	1.000031563	0.8220456(25)	[47]
	0.95866015	1.000062459	0.8220432(25)*	² H(D)
			0.8220445(10)	[50]ABMR
			0.8220454(25)	[51]
	ν(7Li)/ν(3He)			
	0.510164303	1.000031563	3.2564182(98)	[47]
	2.531731524	1.000062459	3.2564085(98)*	² H(D)
			3.2564157(2)	[50]ABMR
			3.2564171(98)	[51]
Na ⁺ water solution/ ³ He	ν(²³ Na)/ν(³ He)			
	0.347233571	1.000520714	2.2174997(111)	[48]
	1.723174611	1.000551603	2.2174962(111)*	² H(D)
			2.2175019(133)	ABMR

Table 5. NMR parameters for calculations of 6/7Li and 23Na nuclear magnetic moments from water solutions.

2.2175065(55)

[52]

3.6. ³He atoms in different chemical environments

It is worth drawing attention to the new spectacular applications of 3-helium spectroscopic achievements. The ³He atom can be inserted into the internal cavities present in fullerene compounds for investigations of the magnetic shielding environments inside cavities. The first developments deal with endohedral fullerenes: ³He@C60 and ³He@C70 [53]. ³He shielding values are 6 and 29 ppm here respectively, relative to the free atom. It means substantial diamagnetic ring currents inside fullerene molecules. It is even possible to incorporate two helium-3 atoms in C70 [54]. Interestingly, the reduction of C60 and C70 fullerenes to its hexaanions ³He2@C60⁻⁶ and ³He2@C70⁻⁶ reduces the magnetic field inside the fullerene diminishing its aromacity [55]. These observations are in good agreement with theoretical predictions [56,57]. ³He NMR spectroscopy was used for probing the small pores in solid substances *e.g.* zeolites [58,59], silica aerogels [60] and nanocavities on the crystal surface powders and single crystals [61]. Besides these chemical uses, it is impossible to omit the huge and still growing biological and medicine applications of 3-helium MRI methods. A few remarks about these studies will be added in the conclusion section of this paper.

4. Conclusions

In this review we have shown the main achievements of the NMR method for establishing nuclear magnetic moments of different nuclei which were performed in the gas phase using ³He atoms. It was established that this method is distinguished by its high degree of accuracy and precision. NMR measurements in high magnetic fields, in spectrometers of advanced technology and sophisticated quantum calculation methods leads to unprecedented results. The final nuclear magnetic moment was identified with at least 0.01% accuracy. The interpolation NMR parameters to the zero-point pressure of gases deals with well-defined chemical species, atoms and molecules. The shielding corrections for these species are often known with great quality from sophisticated theoretical calculations. The experimental conditions in liquid solutions are quite different. The most common water solutions are often complicated systems where cations and anions are solvated by different numbers and time changing water dipoles. The calculation of shielding values of these different solute compositions is a complicated task and only limited results are available. References suggested for NMR measurements of nuclear magnetic moments are: ¹H (proton), ²H (deuteron) and ³He (helion). Experiments performed in the gaseous phase are strongly recommended. The Helion (³He) nuclear magnetic moment belongs to the more accurately known values among all nuclei in the Periodic Table with 1.2×10⁻⁸ relative standard uncertainty. Despite this, we hope that newly planed experiments by physicists, using Penning-trap methods in combination with laser cooling, will provide even better results in the near future [62]. Helium-3 has unique properties that currently makes it very useful in several fields: cryogenic properties useful in low temperature physics, magnetic resonance imaging (MRI) with hyperpolarisd atomic nuclei in medicine, and in fast neutron high sensitivity for 3-helium detectors. The gaseous helium-3 magnetic resonance method is used even more in cryogenic environments [63] and as a probe of the nature solid-superfluid interface [64]. ³He can be hyperpolarized by spin-exchange optical pumping and other methods. On the other hand, the helium atom with the ³He nucleus can be used as a probe of electron densities inside macromolecule compounds if only NMR spectra can be measured for encapsulated helium-3 species. Finally, local magnetic fields in liquid crystals utilising ³He NMR spectroscopy are also known from research [65]. More valuable and prospective are MRI investigations with hyperpolarized helium-3 atoms in medical treatment firstly demonstrated in the lung images of a guinea pig [66]. This unique chemical nucleus and/or atom is a definitely good probe of the matter being investigated. It is truly fascinating to observe the discovery of new and surprising purposes of helium-3 in environmental research. We are

convinced that this small and curious species will find several spectacular applications in chemistry, physics and biology in the near future as well.

Upon completion of this paper, we recognize a very recent publication by Pachucki *et al.* (2021) [67] on the QED effects in calculations of ³He shielding constant. The final result gained in accuracy is there: $\sigma(^{3}\text{He})=59.967029(23)\mu\text{N}$ in good agreement with previous result mentioned in this work. New value don't influence essentially of helium-3 nuclear magnetic moment.

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