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Nuclear magnetic dipole moments of ^{75}As, ^{121}Sb, and ^{123}Sb from *ab initio* calculations of NMR shielding constants and existing NMR experiments

Andrej Hurajt

Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava,
Mlynská dolina, Ilkovičova 6, 842 15 Bratislava, Slovak Republic

Dariusz Kędziera and Anna Kaczmarek-Kędziera

Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina 7, 87-100 Toruń, Poland

Andrej Antušek[*]

Slovak University of Technology in Bratislava, ATRI, Faculty of Materials Science
and Technology in Trnava, J. Bottu 25, 917 24 Trnava, Slovak Republic

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Accurate NMR shielding constants of As and Sb in AsF_6^-, AsO_4^{3-}, $SbCl_6^-$, and SbF_6^- complexes were calculated using the nonrelativistic coupled-cluster method and relativistic four-component density functional theory (DFT). Magnetic dipole moments of ^{75}As, ^{121}Sb, and ^{123}Sb nuclei were rederived and the new recommended reference nuclear magnetic dipole moments are $\mu(^{75}\mathrm{As}) = 1.437\,11(4)\mu_N$, $\mu(^{121}\mathrm{Sb}) = 3.355\,40(33)\mu_N$, and $\mu(^{123}\mathrm{Sb}) = 2.543\,89(25)\mu_N$, correcting systematic errors of up to $0.008\mu_N$ in previous reference values.

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I. INTRODUCTION

The magnetic dipole moment of the atomic nucleus is one of its fundamental properties and it carries important information about the nuclear structure [1,2]. Direct measurements of the nuclear magnetic dipole moments on the bare nuclei are rare, limited to the lightest nuclei, protons, and ^{3}He [3–5]. For heavier nuclei, magnetic dipole moments are measured using nuclear magnetic resonance (NMR) techniques and to derive the nuclear magnetic dipole moment value from the NMR experiment, an accurate NMR shielding constant for the nucleus of interest in the measured compound is required [6]. Historically, only a rough approximation to NMR shielding—the so-called diamagnetic correction—was available. The nuclear magnetic dipole moments based on this approximation [7] contained significant systematic errors which can be illustrated by a spectacular failure of the diamagnetic correction for transition metal complexes (see Fig. 3 of Ref. [8]). Accurate NMR shielding constants became available with the development of *ab initio* methods [9,10], and it led to the refinement of nuclear magnetic moments [6,11]. The majority of magnetic dipole moments of stable nuclei for s, p, d elements were corrected during the last decade. Accurate magnetic dipole moments found their application in NMR spectroscopy [12], hyperfine experiments [13,14], and as the reference nuclear magnetic moments for series of radioactive nuclei [15]. Presently, a new edition of the nuclear data tables by Stone [16] contains corrected magnetic dipole moment values based on NMR experiments and the accurate *ab initio* NMR shielding calculations by Antušek, Jaszuński, Jackowski, and co-workers [6,8,11,14,17–19], Vaara *et al.* [20], and Skripnikov *et al.* [13]. Arsenic and antimony are among the few nuclei which were omitted in the investigations [21].

Arsenic and antimony are somewhat neglected elements in NMR spectroscopy [22] and only a few NMR studies of arsenic and antimony compounds are available in the chemistry literature [23,24]. In physics, antimony nuclei are attractive for hyperfine interactions due to their high spin [25]. In a recent study [2] nuclear magnetic dipole moments of antimony nuclei $^{112-133}$Sb were measured by collinear laser spectroscopy and the series was used as a test of *ab initio* nuclear structure models. Owing to the absence of a reliable reference, the derived series of magnetic moments was based on the reference moment of the stable ^{123}Sb nucleus linked to the original experiment [26] and determined using an obsolete inaccurate diamagnetic correction.

The aim of this paper is to refine the magnetic dipole moments of ^{75}As, ^{121}Sb, and ^{123}Sb nuclei and establish a new reference based on the modern IUPAC (International Union of Pure and Applied Chemistry) NMR standards [27] and accurate *ab initio* computational protocols for NMR shielding constants. IUPAC NMR standards for arsenic and antimony are prepared as acetonitrile solutions of $NaAsF_6$ and $KSbCl_6$ salts [27] which lead to the formation of AsF_6^- and $SbCl_6^-$ complexes. Our study is augmented by an analysis of AsO_4^{3-} and SbF_6^- complexes (constituents of water solutions of Na_3AsO_4 and $NaSbF_6$ salts) which were used in the original 1950s experiments [26,28]. We assume that arsenic and antimony complexes in these solutions are separated from their counterions.

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[*] andrej.antusek@stuba.sk

II. METHODS

In order to obtain an accurate approximation of the NMR shielding constants for As and Sb nuclei in selected arsenic and antimony complexes, electron correlation and relativistic effects have to be incorporated [9,29]. We employ previously developed computational protocols [8,14] which evaluate electron correlation effects using the nonrelativistic coupled-cluster (CC) method [30,31] and relativistic effects from the relativistic four-component density functional theory of Dirac-Kohn-Sham (DKS) [32,33]. The reference nonrelativistic NMR shielding constants are evaluated by the coupled-cluster method with single and double excitations (CCSD) and the noniterative incorporation of triple excitations [CCSD(T)]. In nonrelativistic density functional theory (DFT) and relativistic DKS method we employ the Becke three-parameter Lee-Yang-Parr (B3LYP) functional [34–37]. Based on these methods, three approximations of NMR shielding constants are derived:

Approximation A1: The NMR shielding constant calculated using the relativistic four-component Dirac-Hartree-Fock (DHF) is corrected by the electron correlation contribution Δ_{corr} evaluated at the nonrelativistic level as the difference between CCSD(T) and Hartree-Fock (HF) shielding.

Approximation A2: The nonrelativistic CCSD(T) NMR shielding constant is corrected by a relativistic correction Δ_{rel} evaluated as the difference between the DKS/B3LYP value and its nonrelativistic limit obtained by increasing the speed of light by a factor of 20.

Approximation A3: This approximation is based on the tailored DFT functional (we denote it as B3LYP-x) with the Hartree-Fock exchange admixture scaled to reproduce the reference nonrelativistic CCSD(T) value. This tailored functional is subsequently transferred to the four-component framework and the DKS/B3LYP-x NMR shielding constant represents the third approximation.

In nonrelativistic calculations of the NMR shielding constants we used the Dunning basis set series [38–41]. In coupled-cluster calculations all electrons were correlated. In relativistic four-component calculations, fully uncontracted versions of Dunning basis sets were used and the restricted magnetic balance procedure [33] for generating a small component basis set was employed. The Gaussian charge model [42] of the nucleus was used in all relativistic calculations. In all NMR shielding calculations, gauge including atomic orbitals (GIAO) were used [33,43,44].

The influence of the solvent on NMR shielding was taken into account using the polarized continuum model (PCM) [45] and evaluated using the DKS/B3LYP level of theory [8]. Two kinds of solvents were modeled, a water solvent with a dielectric constant $\epsilon = 78$ for AsO_4^{3-} and SbF_6^- complexes, and acetonitrile with $\epsilon = 36$ applied in the case of AsF_6^- and $SbCl_6^-$ complexes. The solvation effects are incorporated as an additive term (Δ_{PCM}) which was obtained as the difference between the DKS/B3LYP NMR shielding constants computed with and without the PCM model.

The coupled-cluster calculations were realized with the CFOUR program [46], and for the nonrelativistic DFT calculations the ORCA software package [47] was used. All relativistic calculations were carried out in the RESPECT program [48]. The basis sets were taken from the Basis Set Exchange site [49].

III. RESULTS AND DISCUSSION

A. Structure optimization of complexes

As a prerequisite for the NMR shielding calculations, a structure optimization was performed for all model complexes, confirming a tetrahedral shape (T_d point group) for AsO_4^{3-} and an octahedral shape (O_h point group) for AsF_6^-, SbF_6^-, and $SbCl_6^-$ complexes.

This optimization process encompassed the utilization of the density functional theory (DFT) with the B3LYP functional including a dispersion correction with the Becke and Johnson dumping (D3-BJ) [50], with def2-XZVP (X=T,Q) [51,52] basis sets. Scalar relativistic effects were incorporated by the effective core potential (ECP) [53]. Additionally, two wave-function-based methods with the relativistic Douglas-Kroll-Hess (DKH2) Hamiltonian [54,55] were used: the second-order perturbation theory with resolution of identity (DKH2-RI-MP2) [56] and coupled cluster [DKH2-CCSD(T)] [57,58]. These methods were combined with the Dunning correlation consistent polarized valence cc-pVXZ-DK (X = T,Q) basis sets contracted for the Douglas-Kroll (DK) relativistic calculations [39,59]. The influence of solvents (water and acetonitrile) on the bond lengths of the complexes was modeled for DFT and DKH2-RI-MP2 methods utilizing the polarized continuum model [60]. All structure optimizations were carried out in the ORCA software package [47].

The bond lengths resulting from the optimization procedures for all used electronic structure models are collected in Table I. The DFT method systematically overestimates bond lengths in comparison with second-order Møller-Plesset (MP2) and CC methods. The experimental data for the bond lengths of the complexes in respective solvents are not available. Therefore for a comparison we include crystallographic experimental data [61–64]. Although complexes in solvents and in crystals experience different environments, the crystallographic data and optimized bond lengths are in good agreement with discrepancies of $\approx 10^{-2}$ Å. The analysis shows a low sensitivity of the optimized bond lengths on the solvent with an exception of the AsO_4^{3-} complex where the influence reaches about −0.02 Å.

The structures optimized with the DKH2-CCSD(T)/cc-pVQZ-DK method were selected for the calculations of NMR shielding constants and the bond-length uncertainties determined in this section are considered in the final evaluation of the NMR shielding error bars.

B. NMR shielding constants

The NMR shielding constants calculated for basis set series and all methods are collected in separate tables for arsenic (Table II) and antimony complexes (Table III).

For the analysis of the basis set incompleteness error we calculated the NMR shielding constants for the series of Dunning basis sets with increasing cardinal number X. The core-valence Dunning basis set family cc-pCVXZ (X=D,T,Q) was used for arsenic [38] and the uncontracted cc-pwCVXZ-

TABLE I. Bond lengths in Ångstroms for As and Sb complexes.

	As-O in AsO_4^{3-}		As-F in AsF_6^-		Sb-F in SbF_6^-		Sb-Cl in $SbCl_6^-$	
Method	TZ	QZ	TZ	QZ	TZ	QZ	TZ	QZ
DFT/B3LYP	1.7401	1.7380	1.7524	1.7517	1.9100	1.9074	2.4135	2.4135
DFT/B3LYP+PCM[a]	1.7135	1.7120	1.7498	1.7491	1.9072	1.9046	2.4110	2.4108
DK-RI-MP2	1.7202	1.7159	1.7317	1.7278	1.8993	1.8851	2.3724	2.3659
DK-RI-MP2+PCM[a]	1.6969	1.6922	1.7294	1.7255	1.8968	1.8825	2.3703	2.3637
DK-CCSD(T)	1.7183	1.7128	1.7282	1.7241	1.8957	1.8874	2.3839	2.3769
Expt.		1.70[b]		1.702[c]		1.857(1)[d] 1.921(1)[d]		2.389(7)[e] 2.401[e]

[a] See the text for the modeled solvent.
[b] Reference [61].
[c] Reference [62].
[d] Reference [63].
[e] Reference [64].

TABLE II. Isotropic NMR shielding σ_{iso} in ppm of As in AsO_4^{3-} and AsF_6^- complexes. Convergence with the basis set. DZ = cc-pCVDZ/cc-pVDZ, TZ = cc-pCVTZ/cc-pVTZ, QZ = cc-pCVQZ/cc-pVQZ; for relativistic methods (DHF, DKS) all basis were uncontracted. See the text for the basis set details.

	As in AsO_4^{3-}			As in AsF_6^-		
Method	DZ	TZ	QZ	DZ	TZ	QZ
HF	1275.4	1257.3	1243.7	1666.7	1668.8	1665.7
CCSD	1226.3	1183.3	1158.7	1583.3	1558.3	1547.6
CCSD(T)	1212.4	1169.4	1142.8	1566.9	1536.8	1523.4
DFT/B3LYP	1054.4	1033.2	1008.2	1404.4	1395.6	1385.7
DFT/B3LYP-x	1175.4	1158.9	1140.5	1532.9	1530.8	1524.5
DHF	1445.1	1476.0	1473.1	1888.9	1909.7	1909.8
DKS/B3LYP	1187.0	1217.2	1210.3	1594.7	1623.9	1623.1
DKS/B3LYP-x	1327.3	1360.8	1356.5	1737.5	1765.0	1765.2
DKS/B3LYP nr lim	988.2	1012.7	1009.7	1362.0	1385.3	1386.5
DKS/B3LYP+PCM	1167.1	1196.6	1191.8	1595.3	1623.8	1623.4
Δ_{corr}	−63.0	−87.9	−100.9	−99.8	−132.0	−142.3
Δ_{rel}	198.8	204.5	200.6	232.7	238.6	236.6
Δ_{PCM}	−20.1	−20.6	−18.5	0.6	−0.1	0.3

TABLE III. Isotropic NMR shielding σ_{iso} in ppm of Sb in $SbCl_6^-$ and SbF_6^- complexes. Convergence with the basis set. TZ/DZ = cc-pwCVTZ-DK3/cc-pVDZ, TZ = cc-pwCVTZ-DK3/cc-pVTZ, QZ = cc-pwCVQZ-DK3/cc-pVQZ; for relativistic methods (DHF, DKS) all basis were uncontracted. See the text for the basis set details.

	Sb in $SbCl_6^-$			Sb in SbF_6^-		
Method	TZ/DZ	TZ	QZ	TZ/DZ	TZ	QZ
HF	2964.0	2974.5	2978.3	3314.7	3339.6	3349.2
CCSD	2757.3	2773.9	2784.9	3074.8	3115.9	3127.9
CCSD(T)	2724.6	2736.5	2744.6	3037.8	3074.9	3083.4
DFT/B3LYP	2434.4	2456.2	2452.9	2779.6	2806.5	2812.9
DFT/B3LYP-x	2737.5	2742.7	2744.0	3045.5	3076.1	3082.9
DHF	4273.9	4278.5	4280.1	4294.3	4320.7	4329.4
DKS/B3LYP	3991.4	3992.3	3994.8	3759.8	3787.2	3796.9
DKS/B3LYP-x	4122.1	4129.2	4132.2	4056.1	4085.4	4095.5
DKS/B3LYP nr lim	2495.7	2511.5	2518.2	2872.1	2895.4	2904.2
DKS/B3LYP+PCM	3962.5	3968.2	3973.0	3767.9	3796.8	3806.7
Δ_{corr}	−239.4	−238.0	−233.7	−276.9	−264.7	−265.8
Δ_{rel}	1495.7	1480.8	1476.6	887.7	891.8	892.7
Δ_{PCM}	−28.9	−24.1	−21.8	8.1	9.6	9.8

TABLE IV. Isotropic NMR shielding constants in ppm for A1, A2, and A3 approximations, the uncertainties from various sources, and the final isotropic NMR shielding constants of As and Sb. All values are for the quadruple-ζ basis set, with the PCM correction added. See the text for the details of the error bar evaluation.

	As in AsO$_4^{3-}$	As in AsF$_6^-$	Sb in SbCl$_6^-$	Sb in SbF$_6^-$
A1: DHF+Δ_{corr}+Δ_{PCM}	1353.7	1767.8	4024.6	4073.4
A3: DKS/B3LYP-x+Δ_{PCM}	1338.0	1765.5	4110.4	4105.3
A2: CCSD(T)+Δ_{rel}+Δ_{PCM}	1324.8	1760.3	4195.5	3985.9
e_{bs}	−26.6	−13.4	8.1	8.5
e_{cc}	−15.9	−24.2	−40.3	−44.5
e_{add}	15.7	5.2	85.1	119.4
e_{struct}	16.8	1.0	24.3	17.0
Final σ_{iso}	1338 ± 39	1766 ± 28	4110 ± 98	4105 ± 129

DK3 (X=T,Q) basis set series [39] were used for antimony. Other elements (O, F, Cl) were described with valence-type cc-pVXZ (X=D,T,Q) basis sets [40,41]. Core-valence and valence basis sets with the same cardinal number were combined. The double-ζ basis set for antimony is not available, therefore the smallest basis set combination used for antimony complexes was uncontracted cc-pwCVTZ-DK3 for Sb and cc-pVDZ for F and Cl atoms (denoted as TZ/DZ in tables). The convergence analysis with the basis set cardinal number suggests that the NMR shielding constants calculated for the quadruple-ζ basis set are close to the basis set limit for all presented methods and all considered complexes.

In comparison to CCSD(T) reference NMR shielding constants, the DFT/B3LYP method systematically underestimates NMR shieldings. This DFT error was eliminated for the tailored B3LYP-x functional with a Hartree-Fock admixture of 0.53 for AsF$_6^-$, 0.55 for SbF$_6^-$, and 0.61 for AsO$_4^{3-}$ and SbCl$_6^-$ complexes, adjusted to reproduce CCSD(T) quadruple-ζ shieldings. We recall that in the standard B3LYP functional the HF exchange admixture of 0.20 was chosen to reproduce the properties for a set of molecules [34].

The final approximations A1, A2, and A3 for the NMR shielding of arsenic and antimony are collected in Table IV. Our final NMR shielding constants are based on the DKS/B3LYP-x method (approximation A3). Despite the fact that the incorporation of correlation and relativistic effects is very different in the three presented NMR shielding approximations, the span of NMR shielding constants obtained from these approximations is small in comparison with their absolute values, and NMR shielding constants lie in ranges of 30, 7, 180, and 120 ppm, for AsO$_4^{3-}$, AsF$_6^-$, SbCl$_6^-$ and SbF$_6^-$ complexes, respectively. Not only the consistency of these three approximations justifies our approach. Relativistic four-component coupled-cluster NMR shielding constants for a few systems containing heavy atoms are available in the literature [13,65,66] and the derived magnetic moments are consistent with our predictions based on the A1, A2, and A3 approximations [8,14,67].

To estimate the accuracy of our NMR shielding constants we analyzed uncertainties from various sources (Table IV). We considered the basis set incompleteness error e_{bs} estimated as the difference between quadruple-ζ and triple-ζ values of NMR shielding at the CCSD(T) level of theory. The error due to coupled-cluster expansion truncation e_{cc} is estimated as the difference between CCSD(T) and CCSD NMR shielding values for the quadruple-ζ basis set. The systematic error due to the correlation and relativistic effects' nonadditivity e_{add} is estimated as max{|A3-A1|,|A3-A2|}. We note that NMR shielding constants evaluated using approximation A3 are between approximations A1 and A2 except for the SbF$_6^-$ complex where approximation A3 slightly overshoots approximation A1. The bond-length uncertainties of 0.02 Å estimated from model structures (Table I) are projected to the shielding constants' structural error e_{struct}, which is evaluated from the additional DKS/B3LYP-x calculations with the quadruple-ζ basis set for complexes with symmetrically contracted and elongated bond lengths. The total error is evaluated as $e_{\text{total}} = \sqrt{e_{\text{bs}}^2 + e_{\text{cc}}^2 + e_{\text{add}}^2 + e_{\text{struct}}^2}$.

We note that for the solvent effects we tested also the explicit solvent model (see, e.g., Ref. [8]) with water or acetonitrile solvent molecules in the first solvation shell of AsO$_4^{3-}$, AsF$_6^-$, SbCl$_6^-$, and SbF$_6^-$ complexes. The explicit solvent model gives results consistent with the PCM model contribution Δ_{PCM}. Differences are related to the change in the bond-length complexes upon the influence of solvent molecules. This uncertainty is covered by the structural error e_{struct}, therefore the separate error for the solvent effects was not introduced.

There is only limited experimental data available for comparison. The observed chemical shift between the AsF$_6^-$ and AsO$_4^{3-}$ complexes is 369 ppm [23], which is consistent with our theoretical chemical shift 406 ± 48 ppm.

C. Nuclear magnetic dipole moments

We derive the magnetic moment $\mu(\mathrm{X})$ of the nucleus X ($\mathrm{X} = {}^{75}\mathrm{As}$, ${}^{121}\mathrm{Sb}$, ${}^{123}\mathrm{Sb}$) taking the proton magnetic moment $\mu(\mathrm{p}) = 2.792\,847\,344\,62(\pm 0.000\,000\,000\,82)\mu_N$ [4] as the reference, and following the equation [6]

$$\mu(\mathrm{X}) = \frac{I_{\mathrm{X}}}{I_{\mathrm{p}}} \frac{\nu(\mathrm{X})}{\nu(\mathrm{p})} \frac{[1 - \sigma_{\text{iso}}(\mathrm{p})]}{[1 - \sigma_{\text{iso}}(\mathrm{X})]} \mu(\mathrm{p}), \tag{1}$$

where $\sigma_{\text{iso}}(\mathrm{X})$ represents our *ab initio* NMR shielding constants, and I_{X} and I_{p} is the spin of the nucleus X and proton, respectively, $\frac{\nu(\mathrm{X})}{\nu(\mathrm{p})}$ is the IUPAC NMR standard frequency ratio with respect to liquid tetramethyl silane (TMS) [27] and

TABLE V. Nuclear magnetic dipole moments of ^{75}As, ^{121}Sb, and ^{123}Sb in nuclear magnetons μ_N compared with previous values, and input parameters—frequency ratios and σ_{iso}.

Nucleus	Spin	Compound	Standard[a]	Freq. ratio	σ_{iso}	μ/μ_N	Ref. experiment	Ref. shielding
^{75}As	3/2−	AsF_6^-	^{1}H in TMS	0.17122614	1766 ± 28	+1.43711(4)[e,f]	Harris 2002 [27]	This work
		AsO_4^{3-}	^{1}H in H_2O	0.17129(3)	1338 ± 39	+1.4371(3)[f]	Jeffries 1952 [28]	This work
		AsO_4^{3-}	^{1}H in H_2O	0.17129(3)	2295[b]	+1.4383(3)	Jeffries 1952 [28]	Stone 2019 [16]
		AsO_4^{3-}	^{1}H in H_2O	0.17129(3)	3167[c]	+1.439475(65)	Jeffries 1952 [28]	Raghavan 1989 [7]
		$HAsO_4^{2-}$	^{2}D in D_2O	1.11569(5)	2832[d]	+1.43893(8)	Ting 1953 [70]	Ting 1953 [70]
		AsO_4^{3-}	^{1}H in H_2O	0.17129(3)	0	+1.4350(3)	Jeffries 1952 [28]	Uncorrected
^{121}Sb	5/2+	$SbCl_6^-$	^{1}H in TMS	0.23930577	4110 ± 98	+3.35540(33)[e,f]	Harris 2002 [27]	This work
		SbF_6^-	^{23}Na	0.90480(9)	4105 ± 129	+3.3558(6)[f]	Proctor 1951 [26]	This work
		SbF_6^-	^{23}Na	0.90480(9)	4556[b]	+3.3580(16)	Proctor 1951 [26]	Stone 2019 [16]
		SbF_6^-	^{23}Na	0.90480(9)	6378[c]	+3.3634(3)	Proctor 1951 [26]	Raghavan 1989 [7]
		SbF_6^-	^{23}Na	0.90480(9)	0	+3.3427(6)	Proctor 1951 [26]	Uncorrected
^{123}Sb	7/2+	$SbCl_6^-$	^{1}H in TMS	0.129592217	4110 ± 98	+2.54389(25)[e,f]	Harris 2002 [27]	This work
		SbF_6^-	^{2}D in D_2O	0.84423(8)	4105 ± 129	+2.5439(4)[f]	Proctor 1951 [26]	This work
		SbF_6^-	^{2}D in D_2O	0.84423(8)	4556[b]	+2.5457(12)	Proctor 1951 [26]	Stone 2019 [16]
		SbF_6^-	^{2}D in D_2O	0.84423(8)	6378[c]	+2.5498(2)	Proctor 1951 [26]	Raghavan 1989 [7]
		SbF_6^-	^{2}D in D_2O	0.84423(8)	0	+2.5341(4)	Proctor 1951 [26]	Uncorrected

[a] Nuclei other than protons were used as intermediate standards (see original experiments).
[b] σ_{iso} derived from Ref. [16].
[c] σ_{iso} corresponding to the Thomas-Fermi diamagnetic correction.
[d] σ_{iso} corresponding to the Lamb diamagnetic correction.
[e] New recommended reference nuclear magnetic dipole moments.
[f] The sign is not determined in our calculations, taken from Ref. [16].

$\sigma_{\mathrm{iso}}(\mathrm{p}) = 33.480$ ppm is the NMR shielding of proton in liquid TMS [68]. All nuclear magnetic moments are measured in units of nuclear magneton μ_N [69].

New magnetic dipole moments of ^{75}As, ^{121}Sb, and ^{123}Sb nuclei are compared with previous values in Table V and visualized in Fig. 1. The magnetic dipole moments based on our NMR shielding constants and IUPAC NMR standards significantly improve upon previous values, eliminating the long-standing systematic error. Generally, uncorrected magnetic dipole moments from the original experiments [26,28] systematically underestimate the magnetic moments. On the other hand, the application of diamagnetic corrections (Thomas-Fermi or Lamb) [7,70] led to overestimated values of the magnetic moments. Diamagnetic corrections provide only crude approximations for the diamagnetic part of NMR shielding, neglecting negative the paramagnetic part—overestimated shielding leads to an overestimated magnetic moment.

For comparison we derived nuclear magnetic dipole moments from the original experimental data [26,28] for AsO_4^{3-} and SbF_6^- complexes applying our *ab initio* NMR shielding constants. (In the derivation we corrected the 1950s value of proton magnetic moment to the present value.) These corrected moments are practically identical with our magnetic moments based on modern IUPAC standards for AsF_6^- and $SbCl_6^-$. This comparison suggests that in the early 1950s NMR experiments the measurements of the resonance frequencies were sufficiently accurate, with the only obstacle to derive accurate magnetic dipole moments was the inaccurate approximation for NMR shielding available at that time.

We note that the error bars of rederived magnetic dipole moments from the original experiments of AsO_4^{3-} and SbF_6^- are dominated by the declared (and it seems overestimated) error for the resonance frequency measurement. On the other hand, in the magnetic moment values based on IUPAC standards for AsF_6^- and $SbCl_6^-$ the IUPAC frequency ratios have a sub-ppm accuracy, therefore they are considered as exact in the evaluations of magnetic moment error bars. The error bars in this case are dominated by the uncertainty in the NMR shielding constants.

IV. CONCLUSIONS

The presented accurate values of nuclear magnetic dipole moments with reduced error bars, based on high-level *ab initio* NMR shielding calculations and IUPAC NMR frequency measurements, redefine the reference nuclear magnetic moments of ^{75}As, ^{121}Sb, and ^{123}Sb. These magnetic dipole moments provide reliable references in nuclear physics, becoming the reference for magnetic moments in the isotopic series of radioactive/exotic nuclei. In NMR spectroscopy the new values make possible the direct measurement of NMR shielding in experiments for arsenic and antimony compounds. Our NMR shielding constants define absolute NMR shielding scales for arsenic and antimony with small uncertainties of about 4% of their chemical shift ranges.

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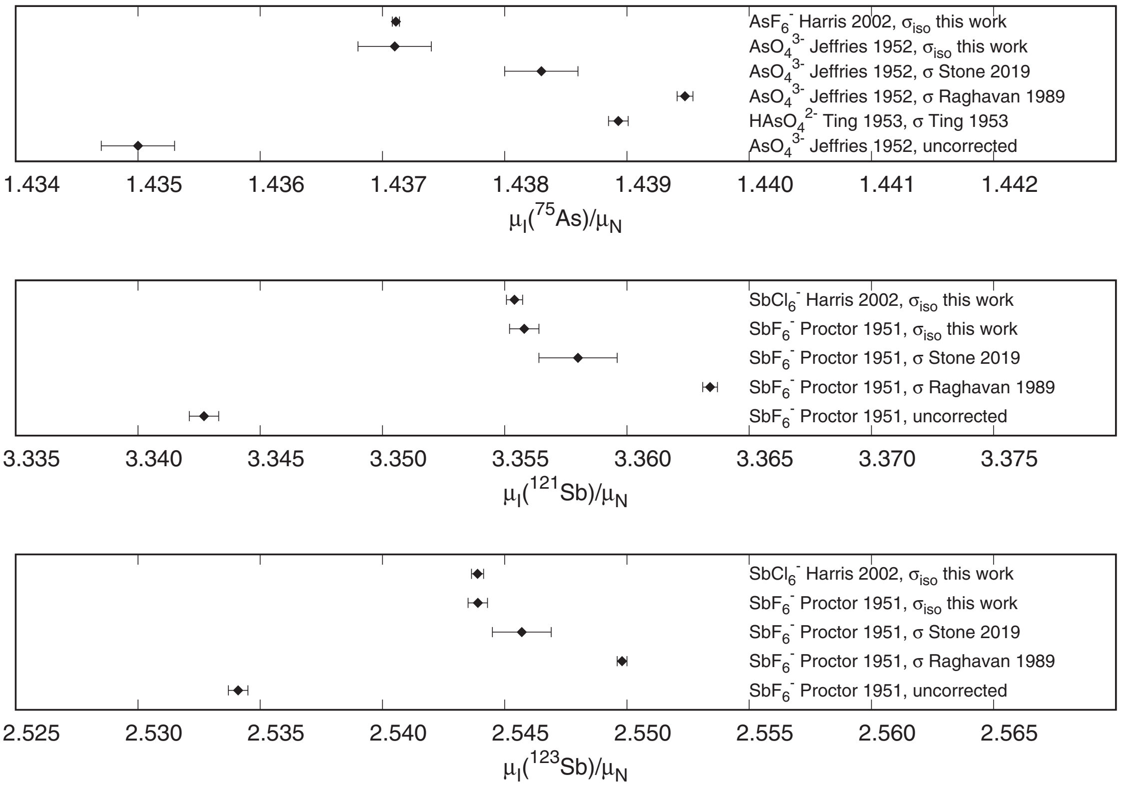

FIG. 1. New recommended reference nuclear magnetic dipole moments for ^{75}As, ^{121}Sb, and ^{123}Sb (on the top of each plot) based on IUPAC NMR experiments and *ab initio* NMR shielding constants compared with other available values. The reference compound, the source experiments [26–28,70], and the source of correction/shielding [7,16,70] are provided. Plots are not in the same scale.

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