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Isotope shift and hyperfine structure in the atomic spectrum of hafnium by laser spectroscopy

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The isotope shift and the hyperfine structure of 14 spectral lines of Hf I were investigated using high-resolution laser spectroscopy of a well-collimated beam of Hf atoms. The hyperfine splitting constants A and B of the electronic states $^5G_5, \ldots, {}^5G_2, {}^5F_3$ of the excited configuration $5d^26s6p$ and of some electronic states of $5d6s^26p$ were obtained for the two stable odd isotopes ^{177}Hf and ^{179}Hf. From these data one-electron hyperfine splitting parameters could be deduced, e.g., $a_{6s}=3.08(15)$ GHz for the magnetic dipole part in the case of ^{177}Hf. Our accurate experimental values of the isotope shifts between the stable Hf isotopes 174,176–180 allow a reliable separation of the effect of the specific mass shift and of the field shift for all observed spectral lines. Using the field shift of the 545.29-nm line, which corresponds to an almost pure $5d^26s^2$-$5d^26s6p$ transition, the change in mean-square nuclear charge radius between ^{178}Hf and ^{180}Hf was determined to be $\delta\langle r^2\rangle=0.098(13)$ fm^2. Values of $\delta\langle r^2\rangle$ for the Hf isotopes 174, 176, 177, and 179 referred to ^{178}Hf are also available from the present work.

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I. INTRODUCTION

Experimental studies of isotope shifts and hyperfine splittings of spectral lines of atoms have proven to be an important tool in order to provide information about changes in mean-square nuclear charge radii and about nuclear moments. Large isotopic chains extending far from the line of stability have been investigated in recent years for various elements [1]. These investigations are of particular interest for the range of strongly deformed nuclei allowing a systematic study of the effect of a change in nuclear deformation on the field isotope shift.

The chain of hafnium isotopes seems to be a favorable case for a similar study as all hafnium nuclei are strongly deformed. Recent experimental efforts have been directed towards the production of unstable hafnium isotopes in sufficient amount for measuring optical hyperfine spectra and isotope shifts [2,3]. However, deriving the change in mean-square nuclear charge radii from observed optical isotope shifts requires a knowledge of the specific mass shift which cannot be neglected in comparison to the normal mass shift except for the case of pure s-p or s^2-sp electronic transitions [4]. The purpose of the present paper was to perform a systematic investigation of optical isotope shifts (IS's) of various spectral lines of the hafnium atom ($Z=72$) with high accuracy providing reliable information on the specific mass shift and on the change in mean-square nuclear charge radii.

Our work was performed on the six stable Hf isotopes 174,176–180 using high-resolution laser spectroscopy of a well-collimated beam of Hf atoms as a proper experimental method. The hyperfine structure (hfs) splitting due to the odd isotopes 177 and 179 with nuclear spin of $\frac{7}{2}$ and $\frac{9}{2}$, respectively, has been completely resolved in our experiment allowing a precise determination of the parameters A and B of hfs splitting. Table I shows a compilation of all 14 spectral lines being investigated in our present work with wavelengths between 540 and 800 nm. The data are taken from the tables of Meggers and Moore [5]. Six spectral lines are due to transitions between the ground-state configuration $5d^26s^2$ and the excited configuration $5d^2(a\,^3F)6s(a\,^4F)6p$. The eight remaining lines lead to terms of the excited configuration $5d6s^2(a\,^2D)6p$. A term diagram is shown in Fig. 1.

There exist a few previous investigations of the IS of spectral lines of Hf I [6–9]. In particular, Cajko [6] has obtained the IS between the even isotopes for numerous Hf lines connecting terms of the configuration $5d^26s^2$ with those of $5d^26s6p$. The accuracy of these results was limited by Doppler broadening which, in addition, prevented a determination of the hfs and IS of the two odd Hf isotopes. Recently, an investigation of the hfs and IS of a single line of Hf, the 590.3-nm line, has been performed with high resolution [10]. However, a reliable

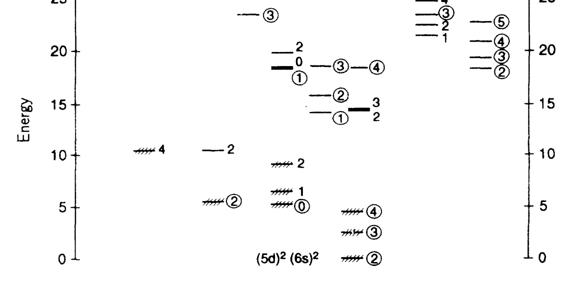

FIG. 1. Part of the energy-level diagram of Hf I. Hatched levels belong to the configuration $5d^26s^2$. Levels with encircled value of J have been investigated within the present work.

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TABLE I. Compilation of data for spectral lines of Hf: T_l is the energy value of the lower even term belonging to configuration $5d^26s^2$; T_u is the energy value of the upper odd term belonging to configuration $5d^26s6p$ (upper six lines) and $5d6s^26p$ (lower eight lines); I is the relative intensity according to Ref. [5]; $\Delta\nu$ is the experimentally observed full width at half maximum for a single hfs line.

λ (nm)	Lower term	T_l (cm^{-1})	Upper term	T_u (cm^{-1})	I	Final term	λ_{obs} (nm)	$\Delta\nu$ (MHz)
545.29	$a\,^3F_4$	4568	$z\,^5G_5$	22 901	300			30
609.87	$a\,^3F_4$	4568	$z\,^5G_4$	20 960	200			30
590.29	$a\,^3F_3$	2357	$z\,^5G_3$	19 293	500			30
732.18	$a\,^1D_2$	5639	$z\,^5G_3$	19 293	150	$a\,^3F_2$	518.2	15
555.06	$a\,^3F_2$	0	$z\,^5G_2$	18 011	1000			15
561.33	$a\,^1D_2$	5639	$z\,^5F_3$	23 449	400	$a\,^3F_2$	426.3	30
555.21	$a\,^1D_2$	5639	$z\,^1F_3$	23 645	1000			40
732.01	$a\,^3F_4$	4568	$z\,^3F_4$	18 225	1000			15
723.71	$a\,^3F_4$	4568	$z\,^3D_3$	18 381	8000			15
543.87	$a\,^3F_2$	0	$z\,^3D_3$	18 381	100	$a\,^3F_3$	623.9	15
618.51	$a\,^3F_2$	0	$z\,^3D_2$	16 163	400	$a\,^3F_3$	724.1	25
713.18	$a\,^3F_2$	0	$z\,^3D_1$	14 018	7000			15
792.08	$a\,^3P_0$	5522	$z\,^3P_1$	18 143	2000			15
551.01	$a\,^3F_2$	0	$z\,^3P_1$	18 143	60	$a\,^1D_2$	799.5	15

and systematic treatment of IS and hfs requires accurate experimental data from a great number of spectral lines which are available from our present work for the case of all stable isotopes of Hf. A small part of our present results has been published previously as preliminary data [11–13].

II. EXPERIMENTAL RESULTS

The light of a tunable single-mode cw dye laser was scattered from the atoms of a well-collimated beam of Hf atoms using the laser-induced fluorescence for detection. The directions of the atomic beam, of the laser beam, and of the beam of the observed light were oriented mutually perpendicular to each other. The atomic beam was produced by heating a cylindrical tantalum oven filled with metallic Hf by means of electron bombardment to a temperature of about 2500 K. At this temperature the lower terms of spectral lines, being above the ground level $a\,^3F_2$ according to Table I, were sufficiently populated by thermal excitation. By collimating the atomic beam with a collimation ratio between 1:60 and 1:120 we obtained a linewidth due to residual Doppler broadening of 15–40 MHz as listed in Table I. We used Hf in natural mixture of isotopes with a relative abundance of 0.2% (174), 5.2% (176), 18.6% (177), 27.3% (178), 13.6% (179), and 35.1% (180).

The tunable dye laser was a commercial linear dye laser (Coherent Radiation 599) pumped by an argon- or by a krypton-ion laser. A relative frequency scale was provided by the transmission peaks of a homemade Fabry-Pérot interferometer of known free spectral range. For some spectral lines the signal-to-noise ratio could be considerably improved by observing the decay of the laser-excited Hf atoms to a final level different from the lower term of the spectral line as indicated in Table I.

Figure 2 shows a complete recording of the hfs and IS of the 545.29-nm line as an example for a spectral line with a large negative IS and with a signal due to the rare isotope 174. Figure 3 represents the experimental result for a spectral line with positive IS. The observed hfs splittings were analyzed using a standard first-order hfs formula [14]. A possible second-order contribution was estimated to be negligible within the accuracy obtained in our experiment. The analysis of the experimental data was greatly simplified in the case of lower terms belonging to the $a\,^3F$ multiplet, as precise values for the hfs constants A and B were available from atomic beam magnetic resonance (ABMR) investigations [15,16]. In addition, this information was particularly useful in checking the accuracy of our relative frequency scale. As can be seen from Figs. 2 and 3 the hfs of the spectral line is almost completely resolved. A somewhat higher amount of overlapping occurred in other spectral lines, in particular those with very small IS, but was taken into account in our analysis by proper computer fits to the experimental line shape.

In Table II we have compiled our results for hfs splitting constants A and B of ^{177}Hf and ^{179}Hf as deduced from our experimental data. The ratios $B(177)/B(179)$ calculated from this data are in complete agreement within limits of error with the more accurate value of 0.884 923(2) obtained by ABMR for the $^3F_2$ ground state [15]. Concerning the ratio $A(177)/A(179)$ small deviations outside limits of error occur for the different terms of Table II. However, all values are covered by the ABMR result for $g_I(177)/g_I(179)$ of $-1.5919(35)$ [15] within error margins preventing us from drawing information on a possible hfs anomaly at the present level of accuracy. In addition, we have included in Table II the results of two recent investigations of the levels $z\,^5G_3$ and $z\,^3D_2$ which agree fairly well with our results. With respect to the discrepancy of $A(177)$ of $z\,^5G_3$ the error bars of Ref. [10] may generally be a little bit too optimistic as their result for $B(179)$ of the level $a\,^3F_3$ misses the

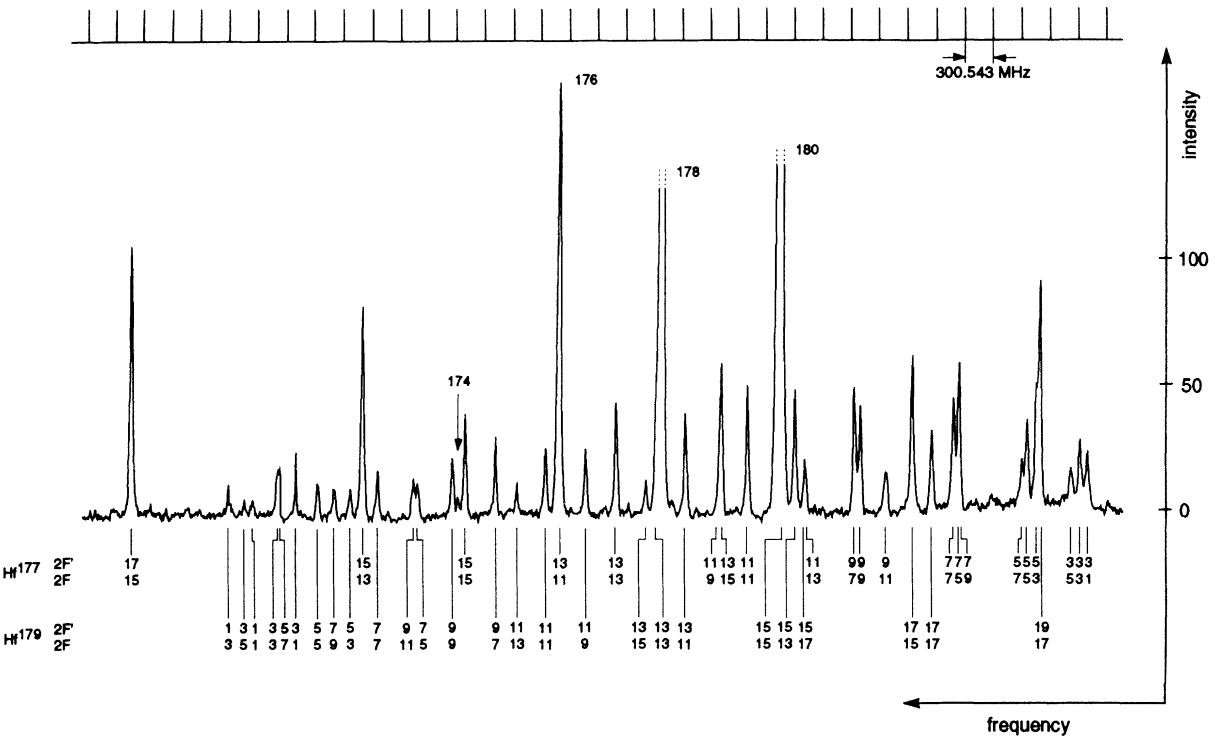

FIG. 2. Example of the recorded spectrum of the 545.29-nm line of Hf due to the transition $5d^26s^2(a\ ^3F_4)$–$5d^26s6p(z\ ^5G_5)$. The signals due to the isotopes 178 and 180 are out of scale. The laser frequency increases from right to left. F' and F are the quantum numbers of total angular momentum of the upper and lower state, respectively.

accurate ABMR value by four times of their error margin.

Table III summarizes our results for the observed IS, the IS for a pair of isotopes A and A' being defined in the usual way as IS $(A,A')=\nu_{A'}-\nu_A$ with $A'>A$. Spectral lines leading to terms of the excited configuration $5d^26s6p$ (the upper part of Table III) are characterized by a large negative IS of about -1000 MHz for 178–180. For most of these spectral lines a signal due to the rare isotope 174 could be observed. For upper terms belonging to the configuration $5d6s^26p$ (the lower part of Table III) the observed value of the IS (178–180) is much smaller and predominantly positive. However, a signal due to ^{174}Hf could not be observed in this case for reasons of in-

TABLE II. Results for hfs splitting constants A and B of levels of configuration $5d^26s6p$ (upper five levels), $5d6s^26p$ (lower six levels), and $5d^26s^2$ (lowest line). The value of B^{177}, marked by an asterisk, has been calculated from the ratio of B values known from ABMR. Term values (in parentheses) are given in units of cm^{-1}.

Term	A^{177} (MHz)	B^{177} (MHz)	A^{179} (MHz)	B^{179} (MHz)	Ref.
$z\ ^5F_3$ (23 449)	250.08(68)	1173.4(5.3)*	−157.72(38)	1326.0(6.0)	
$z\ ^5G_5$ (22 901)	321.10(7)	2191.8(3.8)	−201.87(13)	2477.5(6.5)	
$z\ ^5G_4$ (20 960)	258.60(15)	1838.0(3.9)	−162.55(19)	2081.0(5.2)	
$z\ ^5G_3$ (19 293)	150.95(17)	1826.4(6.5)	−95.14(13)	2070.0(6.8)	
	152.20(40)	1821.6(7.4)	−95.5(1.1)	2055.7(25.1)	[10]
$z\ ^5G_2$ (18 011)	−205.49(30)	2479.1(3.3)	128.74(18)	2801.7(3.1)	
$z\ ^1F_3$ (23 645)	166.39(32)	3006.2(5.0)	−104.89(43)	3392.3(6.2)	
$z\ ^3F_4$ (18 225)	179.21(9)	3276.8(4.4)	−112.69(6)	3701.7(3.6)	
$z\ ^3P_1$ (18 143)	146.28(30)	−694.7(2.5)	−92.03(20)	−785.1(2.3)	
$z\ ^3D_3$ (18 381)	151.40(20)	−26.9(3.6)	−95.14(8)	−30.6(3.5)	
$z\ ^3D_2$ (16 163)	74.49(60)	653.5(7.6)	−46.93(70)	739.8(9.3)	
	75.60(60)	685.0(17.0)	−47.80(60)	756.0(17.0)	[2]
$z\ ^3D_1$ (14 018)	−32.93(30)	269.3(2.0)	20.53(25)	303.8(2.8)	
$a\ ^1D_2$ (5639)	75.47(46)	−805.8(4.1)	−47.68(18)	−905.0(3.2)	

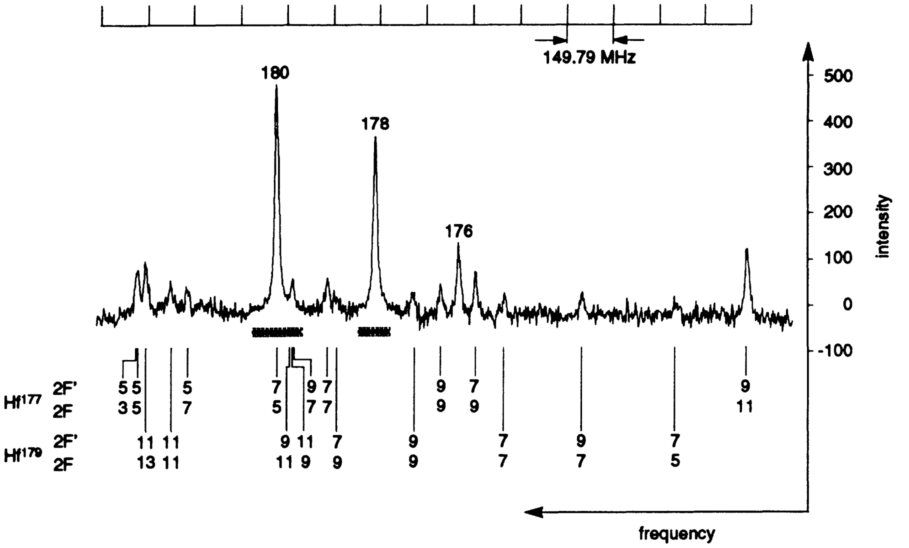

FIG. 3. Example of the recorded spectrum of the 713.18-nm line of Hf due to the transition $5d^26s^2(a\,{}^3F_2)-5d6s^26p(z\,{}^3D_1)$. The sensitivity of the detection circuit was decreased by a factor of 2 in the hatched areas. For further details see the caption of Fig. 2.

tensity. We have included into Table III the results of previous investigations for the 590.29-nm line in order to indicate the considerable deviations to our results. Similar discrepancies occur for part of the other spectral lines marked by an asterisk. But, we have refrained from inserting previous data for all spectral lines into Table III for the sake of clarity.

III. DISCUSSION OF HFS PARAMETERS

The hfs coupling constants A and B are usually interpreted according to the formalism introduced by Sandars and Beck [17], including relativistic effects. Three effective one-electron hfs parameters $a^{k_sk_l}$ ($k_sk_l=01,12,10$) and $b^{k_sk_l}$ ($k_sk_l=02,13,11$) are required for each electron in an open shell. In our case the limited set of experimental values for A and B does not allow a complete determination of all one-electron hfs parameters for a given configuration. Therefore we restrict ourselves to the nonrelativistic limit using the approximation $a_{nl}^{12}=a_{nl}^{01}=a_{nl}$, $a_{nl}^{10}=0$ for the magnetic dipole part, and $b_{nl}^{02}=b_{nl}$, $b_{nl}^{11}=b_{nl}^{13}=0$ for the electric quadrupole part ($l>0$). In all, we are left with three parameters a_{6s},a_{6p},a_{5d} for the magnetic dipole part and with two parameters b_{6p} and b_{5d} for the electric quadrupole part. Our main interest is directed towards a determination of a_{6s}, providing information on the electron density at the origin which is useful in the analysis of the observed isotope shift (see Sec. IV).

As can be seen from Fig. 1 the two excited configurations $5d^26s6p$ and $5d6s^26p$ are by no means well separated in energy and configuration mixing is likely to

TABLE III. Results for isotope shifts of spectral lines of Hf in MHz relative to ^{178}Hf as deduced from our experimental data. For lines marked by an asterisk experimental values of the IS are available from one of Refs. [2,6,8–10].

λ (nm)	Transition	180	179	177	176	174	Ref.
545.29*	$a\,{}^3F_4-z\,{}^5G_5$	−1259.1(3.9)	−452.2(6.1)	−789.6(5.2)	−1097.3(6.7)	−2179.8(6.0)	
609.87*	$a\,{}^3F_4-z\,{}^5G_4$	−1112.5(3.5)	−404.6(7.0)	−690.2(5.8)	−963.1(4.1)		
590.29*	$a\,{}^3F_3-z\,{}^5G_3$	−987.2(4.3)	−362.2(6.2)	−613.1(6.9)	−856.6(3.9)	−1709.0(5.3)	
		−1007.3(9.0)			−860.4(9.0)	−1784(60)	[6]
		−1046.3(18.0)			−854(57)		[9]
		−908(33)					[8]
			−379.1(4.1)	−614.8(8.0)			[10]
732.18	$a\,{}^1D_2-z\,{}^5G_3$	−1010.6(3.5)	−368.8(4.6)	−628.0(5.8)	−876.1(3.5)	−1748.7(4.0)	
555.06*	$a\,{}^3F_2-z\,{}^5G_2$	−959.7(3.7)	−351.8(6.1)	−595.2(4.2)	−832.1(4.4)	−1657.6(4.3)	
561.33*	$a\,{}^1D_2-z\,{}^5F_3$	−955.8(3.5)	−350.5(6.4)	−593.0(9.4)	−825.0(3.8)	−1651.6(7.0)	
555.21	$a\,{}^1D_2-z\,{}^1F_3$	−33.0(3.5)	−18.3(5.3)	−13.3(6.1)	−38.1(3.5)		
732.01	$a\,{}^3F_4-z\,{}^3F_4$	30.9(1.9)	5.8(4.1)	23.7(4.5)	18.9(2.4)		
723.71	$a\,{}^3F_4-z\,{}^3D_3$	135.5(3.5)	42.8(5.0)	90.1(5.0)	107.6(5.0)		
543.87*	$a\,{}^3F_2-z\,{}^3D_3$	238.0(3.5)	82.1(4.3)	151.8(4.5)	200.1(3.5)		
618.51*	$a\,{}^3F_2-z\,{}^3D_2$	311.1(3.0)	106.3(5.0)	199.1(4.0)	263.3(4.0)		
713.18	$a\,{}^3F_2-z\,{}^3D_1$	317.7(3.5)	108.4(5.0)	203.2(5.0)	266.9(3.5)		
792.08	$a\,{}^3P_0-z\,{}^3P_1$	333.2(4.0)	113.8(6.0)	214.0(6.0)	281.9(5.0)		
551.01	$a\,{}^3F_2-z\,{}^3P_1$	378.6(3.5)	131.3(4.8)	240.2(5.0)	320.0(3.5)		

occur. Approximate information on the degree of configuration mixing is available from the work of Wyart [18], taking additionally into account the odd configuration $5d^3 6p$. According to this work, the levels of the ^5G and ^5F multiplet consist of at least 90% of $5d^2 6s 6p$ and contain less than 1% of $5d^3 6p$. On the other hand, the triplet levels in the lower part of Table II show a much higher degree of configuration mixing with 60–70% of $5d 6s^2 6p$, 25–35% of $5d^2 6s 6p$, and about 5% of $5d^3 6p$. For these levels a small change in the coefficient of $5d^2 6s 6p$ may have a large effect on the value of A as a_{6s} is expected to be much larger compared to a_{6p} and a_{5d}.

Our present analysis of the magnetic dipole part is restricted to the five quintet levels of $5d^2 6s 6p$ neglecting configuration mixing. The contributions of the one-electron hfs parameters have been calculated according to the relation [19]

$$A_{\alpha J}=\sum_{i=1}^{4}\{\alpha J\|a_{n_i l_i}[l_i^{(1)}-\sqrt{10}(s_i^{(1)}\times C_i^{(2)})^{(1)}]+\delta_{l_i 0}\, a_{n_i s}s_i^{(1)}\|\alpha J\}/\sqrt{J(J+1)(2J+1)} \tag{1}$$

using standard tensor algebra [20] for the case of pure L-S coupling. αJ is an abbreviation for the complete coupling scheme $([5d^2(a\,^3F)]6s\,^4F)6p\ SLJ$. The coefficients c_{nl} of the three one-electron hfs parameters are listed in Table IV. Solving the five linear equations with three unknown parameters by means of a least-squares-fit procedure, we obtain the following for ^{177}Hf: $a_{6s}=3075(38)$ MHz, $a_{6p}=382(73)$ MHz, $a_{5d}=82(28)$ MHz, where the error margins are the statistical errors provided by the fit routine. As can be seen from Table IV the experimental values of A are reproduced remarkably well with a mean deviation of a few MHz.

Our result for a_{5d} is in agreement with the value $a_{5d}=77$ MHz deduced by Büttgenbach, Dicke, and Gebauer [16] from an analysis of the ground-state configuration $5d^2 6s^2$. In order to estimate the size of systematic errors due to our particular model additional fits have been performed either by omitting one of the five equations of Table IV or by taking into account the different amount of configuration mixing for the five quintet levels. The values of a_{6s} obtained by these fits differ by an amount of about ±150 MHz from the result given above whereas the values of a_{6p} and a_{5d} are covered by the above-mentioned error margins. Therefore, our final result for ^{177}Hf is $a_{6s}=3075(150)$ MHz. Using the nuclear g factor of $g_I=0.2267(2)$ [21] we obtain $a_{6s}/g_I=13.6(7)$ GHz for ^{177}Hf. This value is in good agreement with the value of 13.0(3) GHz deduced for the 6s electron from the optical spectrum of the Lu atom ($Z=71$) [18].

Concerning the electric quadrupole part of the hfs we tried to perform a similar analysis as for the magnetic dipole part by calculating the contributions of the one-electron hfs parameters b_{6p} and b_{5d} for $5d^2 6s 6p$ by means of the relation [19]

$$B_{\alpha J}=-\sum_{i=1}^{3}2b_{n_i l_i}(\alpha J\|C_i^{(2)}\|\alpha J)\sqrt{J(2J-1)/(J+1)(2J+1)(2J+3)}\ . \tag{2}$$

Unfortunately, the five linear equations with two unknown parameters are in contradiction to each other for the case of the five quintet levels, showing that our simple treatment is not adequate. A preliminary estimate of b_{6p} may be obtained from the $^5G_5$ level which, according to the work of Wyart [18], is characterized by an almost pure LS coupling with less than a 0.3% admixture of other configurations. Using the equation $B(^5G_5)=0.3b_{6p}+0.214b_{5d}$ and taking $b_{5d}=4313$ MHz from the analysis of the configuration $5d^2 6s^2$ [16], we get a value of $b_{6p}=4190$ MHz for ^{177}Hf. Obviously, a more refined treatment, including intermediate coupling and configuration mixing, is required in order to interpret all observed B values of the quintet levels.

IV. DISCUSSION OF ISOTOPE SHIFT

The experimental IS values of Table III are the sum of two contributions, the field shift (FS) and the mass shift

TABLE IV. Coefficients of one-electron hfs parameters of the magnetic dipole part of hfs for observed quintet levels of configuration $5d^2 6s 6p$. $\delta A = A_{\text{expt}} - A_{\text{fit}}$.

Term	c_{6s}	c_{6p}	c_{5d}	A_{expt} (MHz)	δA (MHz)
$^5F_3$	0.062 50	−0.018 75	0.722 32	250.1	6.2
$^5G_5$	0.066 67	0.186 67	0.552 38	321.1	−0.2
$^5G_4$	0.037 50	0.250 54	0.664 67	258.6	−6.5
$^5G_3$	−0.020 83	0.346 13	0.866 28	151.0	12.3
$^5G_2$	−0.166 67	0.547 62	1.343 54	−205.5	−11.4

[4]. The latter consists of the trivial normal mass shift (NMS) and the specific mass shift (SMS), both being proportional to $(M_{A'}-M_A)/M_A M_{A'}$, where M_A and $M_{A'}$ are the masses of the two isotopes A and A',

$$\delta\nu_j^{AA'}=F_j\lambda^{AA'}+\delta\nu_j^{AA'}(\text{NMS})+\delta\nu_j^{AA'}(\text{SMS})\ . \tag{3}$$

The FS part in Eq. (3) is the product of a purely nuclear quantity $\lambda^{AA'}$, in essence the change in mean-square nuclear charge radius between the two isotopes, and the electronic factor F_j depending on the particular electronic transition.

At first, the consistency of our experimental IS data was checked by means of the King-plot procedure [22]. In this procedure the modified IS

$$y_j^{AA'}=R\ M_A M_{A'}\,\delta\nu_j^{AA'}/(M_{A'}-M_A)$$

of spectral line j is plotted against the modified IS $x_i^{AA'}$ of the reference line i. R is an arbitrary scaling factor which was set to $R=(M_{180}-M_{178})/M_{178}M_{180}=6.2551\times10^{-5}u^{-1}$ in our case in order to keep the modified IS values near the experimental values. As can be derived from Eq. (3) the points due to different isotope pairs should lie on a straight line in a King plot for each pair of spectral lines. In Fig. 4 we present as an example a King-plot diagram of our IS data taking the 545.29-nm line as a reference line. For some spectral lines the IS values are very close to each other (see Table III). The corresponding data points cannot be distinguished from each other in the presentation of Fig. 4 and have been omitted. All experimental data points fit to a straight line within limits of experimental error with very good agreement demonstrating the consistency of our data with Eq. (3). By means of a least-squares computer fit the two parameters of the straight lines have been determined. Our results for the slope, being equal to the ratio F_j/F_{545} of the electronic factors, are compiled in Table V.

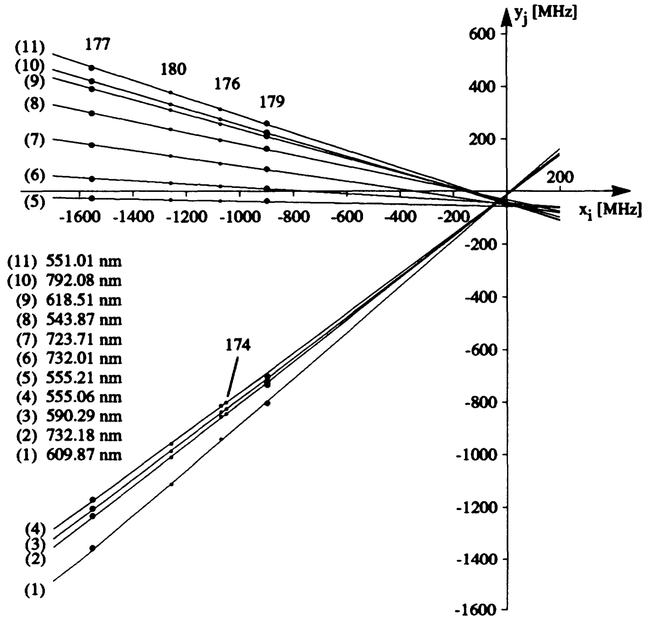

FIG. 4. A King-plot diagram of modified experimental IS values referred to ^{178}Hf using the 545.29-nm line for reference. Full circles: experimental data, the diameter corresponding approximately to the experimental error. The solid lines are the result of a least-squares fit.

In order to separate the contributions of the SMS and of the FS a knowledge of the SMS for a reference line is required. For an electronic transition between configurations s^2 and sp a value of $\delta\nu(\text{SMS})=(0\pm0.5)\delta\nu(\text{NMS})$ is recommended [4]. In our case the transition $5d^26s^2(a\ ^3F_4)$–$5d^26s6p(z\ ^5G_5)$ at 545.29 nm seems to be the best approximation to a pure s^2-sp transition as only small admixtures of other configurations of less than 2.5% are present in the upper and lower level [18]. Therefore the 545.29-nm line was taken as a reference line assuming a SMS as given above. In Table V we have compiled our results for the SMS and the FS of the isotope pair 178-180 for all observed spectral lines.

For spectral lines connecting the configurations $5d^26s^2$ and $5d6s^26p$ (eight lower lines in Table V) the SMS turns out to be about -3 to -5 times the NMS. Such values are not uncommon for the case of a d^2-dp transition [4]. In view of the considerable amount ($\approx25\%$) of admixture of the configuration $5d^26s6p$ to the upper configuration $5d6s^26p$, the SMS of a pure $5d^26s^2$-$5d6s^26p$ transition in Hf is expected to be even somewhat larger if one applies the sharing rule of IS for the case of configuration mixing [23]. For spectral lines connecting the configurations $5d^26s^2$ and $5d^26s6p$ (six upper lines in Table V) the SMS is quite small, but shows a tendency to negative values of about -0.5 to -1 times the NMS. According to the sharing rule this effect may qualitatively be understood as due to the admixture ($\approx10\%$) of the configuration $5d6s^26p$ to the upper configuration $5d^26s6p$.

Additional King plots have been performed using the other lines of the $5d^26s^2$-$5d^26s6p$ group as reference lines. For this case the separation of SMS and FS leads to results which do not differ very much from those given in Table V. Taking a mean value over results obtained with different reference lines is a frequently used procedure [2,6]. However, it seems not to be appropriate in our case due to the increase in configuration mixing in going from the 545.29-nm reference line to other reference lines which is also evident from the decrease of F_j/F_{545} and of the FS in the upper part of Table V.

For the 618.51-nm line the SMS of the isotope pair 178-180 has been determined recently [2] from optical IS measurements to be $-139(12)$ MHz. This value is in complete disagreement with our result in Table V, both results being different by more than a factor of 2. Most probably, the large discrepancy is due to the use of the IS data of Cajko [6] in Ref. [2], which are less accurate than ours and include only the even isotopes, and due to the averaging over a large number of reference lines neglecting the different amount of configuration mixing.

Using the fitted straight lines of the King-plot diagram of Fig. 4 we get identical values of the relative field isotope shift for all spectral lines. These values are compiled in Table VI together with the results of previous investigations. Due to a more refined analysis our final results are slightly different from our preliminary values given in

TABLE V. Results of the King-plot diagram and of the separation of SMS and of FS for isotope pair 178-180 taking the 545.29-nm line for reference.

λ (nm)	F_j/F_{545}	$\delta\nu$ (NMS) (MHz)	$\delta\nu$ (SMS) (MHz)	$\delta\nu$ (FS) (MHz)
545.29	1	18.9	0(10)	−1278(20)
609.87	0.872(27)	16.9	−12(19)	−1114(19)
590.29	0.770(22)	17.4	−18(15)	−984(15)
732.18	0.791(20)	14.1	−11(14)	−1011(14)
555.06	0.750(18)	18.5	−17(13)	−958(13)
561.33	0.756(23)	18.3	−6(15)	−966(16)
555.21	−0.019(18)	18.5	−76(11)	25(11)
732.01	−0.061(13)	14.1	−61(8)	78(8)
723.71	−0.148(18)	14.2	−68(11)	189(12)
543.87	−0.214(16)	18.9	−56(10)	274(11)
618.51	−0.280(17)	16.6	−64(11)	358(11)
713.28	−0.291(18)	14.4	−69(11)	371(12)
792.08	−0.302(22)	13.0	−66(14)	386(14)
551.01	−0.334(18)	18.7	−69(11)	427(12)

Ref. [13], but agree within error margins. Deviations outside limits of error occur between our results and the results of Cajko [6] for the even isotopes, which is not very surprising since the SMS has been completely neglected by Cajko, and his results for different spectral lines show a considerable variation around the average value. With respect to the odd isotopes our results of Table VI clearly demonstrate the large improvement obtained in our work in comparison to previous investigations.

Finally, the absolute value of the change in mean-square nuclear charge radius $\delta\langle r^2\rangle$ will be deduced in the following for the isotope pair 178-180 using the FS value of the 545.29-nm line given in Table V. The electronic factor F_i of Eq. (3) is proportional to the change of probability density of the electron at the origin during the electronic transition. Unfortunately, no relativistic calculation of this quantity is available for the case of Hf. Therefore, we apply the standard semiempirical approach [24] which relates F_i to the nonrelativistic probability density of a single valence ns electron by means of Eq. (4),

$$F_i=\gamma_i f(Z)\pi a_0^3|\psi_{ns}(0)|^2/Z\ . \tag{4}$$

γ_i is the screening factor being defined as the ratio of the change $\Delta|\psi_s(0)|_i^2$ of probability density at the origin for the particular transition i and the quantity $|\psi_{ns}(0)|^2$. The value of γ_i was taken from a nonrelativistic Hartree-Fock calculation by Aufmuth [25] to be $\gamma_i=0.75(5)$ for the 545.29-nm line where the probability density $|\psi_{ns}(0)|^2$ now refers to the $6s$ electron within the configuration $5d^26s6p$. The function $f(Z)$ introduced by Heilig and Steudel [4] is given by $f(Z)=C_{\rm unif}^{AA'}/\delta\langle r^2\rangle_{\rm unif}^{AA'}$ assuming a uniform nuclear charge distribution with radius 1.2 fm $A^{1/3}$. Values of the field isotope shift constant $C_{\rm unif}^{AA'}$ of s electrons are available from improved relativistic calculations [26] yielding $f(Z)=39.89$ GHz/fm^2 for the isotope pair 178-180.

It remains to determine the value of the part $E_{6s}=\pi a_0^3|\psi_{6s}(0)|^2/Z$ of the electronic factor in Eq. (4), which can be obtained from the one-electron hfs parameter a_{6s} given in Sec. III by means of the relation [14,19]

$$a_{6s}=8R_\infty\alpha^2 g_I'\pi a_0^3|\psi_{6s}(0)|^2F_r(1-\delta)(1-\varepsilon)/3Z \tag{5}$$

with R_∞ the Rydberg constant, α the fine-structure constant, and g_I' the nuclear g factor referred to the Bohr magneton. F_r is a relativistic correction factor tabulated in Ref. [14]. δ and ε are small corrections taking into account the effect of the extended distribution of nuclear charge and of nuclear magnetic moment, respectively, on a_{6s}. Inserting numbers into Eq. (5) we arrive at a value of $E_{6s}=0.437(22)$. Using the FS of the 545.29-nm line of 1.278(20) GHz and replacing $\lambda^{AA'}$ by $\delta\langle r^2\rangle^{AA'}$ in Eq. (3) we obtain $\delta\langle r^2\rangle=0.098(13)$ fm^2 for the isotope pair 178-180 as our final result.

Within the standard approach [24] the nuclear parameter of Eq. (3) is usually written as $\lambda^{AA'}=K\delta\langle r^2\rangle^{AA'}$, the additional factor K taking into account the effect of a change in higher-order nuclear charge moments, e.g., $\delta\langle r^4\rangle^{AA'}$, $\delta\langle r^6\rangle^{AA'}$, as introduced by Seltzer [27]. Values of K have been obtained by means of a relativistic

TABLE VI. Relative field isotope shift of Hf isotopes referred to isotope pair 178-180.

178-179	177-178	176-178	174-178	Ref.
0.361(9)	0.625(12)	0.873(16)	1.736(24)	This work
		0.824(8)	1.689(13)	[6]
0.395(85)	0.725(75)	0.826(35)	1.702(51)	[8]

Dirac-Fock calculation using a uniform nuclear charge distribution and a Fermi-type distribution [28] leading to $K=0.950$ for Hf. However, it is not necessary to apply the proper correction in our derivation of $\delta\langle r^2\rangle$ as the function $f(Z)$ is referred to $\delta\langle r^2\rangle_{\text{unif}}$ in our case and not to λ_{unif}.

Recently, the theory of field isotope shift in atoms has been reformulated in a way which avoids the use of the nonrelativistic probability density of the electron at the origin and of the numerous relativistic correction factors of the semiempirical approach [29]. The field isotope shift constant C_s and the hfs parameter a_s are both related to the relativistic probability density N of the electron at the origin. A relativistic calculation has been performed by the authors for a Fermi-type nuclear charge distribution and the tabulated results allow a determination of the nuclear parameter $\lambda^{AA'}$ of Eq. (3) from measured values of the FS and of a_{ns}. Following the approach of Blundell *et al.* [29] for the case of the 545.29-nm line of Hf and applying the K correction mentioned above we deduce a value of $\delta\langle r^2\rangle$ for the isotope pair 178-180 which agrees with the result of the semiempirical approach within a margin of 1%. This agreement corroborates the complete equivalence of the standard semiempirical approach with the correct relativistic treatment, at least within the framework of a single s electron outside closed shells.

In Table VII we have compiled the results of $\delta\langle r^2\rangle$ for the isotope pair 178-180 obtained by different experimental methods. Our result is in good agreement with the values deduced from electronic and muonic x-ray IS measurements. A large deviation occurs with respect to the result of an investigation of the optical IS in Hf II and to a similar value obtained from optical IS measurements in Hf I [7]. In either case $\delta\langle r^2\rangle$ has been determined using an electronic factor deduced by applying the Fermi-Goudsmit-Segré (FGS) formula [14] to the observed term energies of Hf II yielding $E_{6s}=0.63(2)$ [33]. This result is quite different from the value of $E_{6s}=0.437(22)$ used in our analysis and deduced from the hfs parameter a_{6s}. Probably, the FGS formula, being originally derived for the one-electron case, is only a poor approximation in the three-electron case $5d^2nl$ of Hf II. On the other hand, the screening factor γ_i of Eq. (4) obtained from a nonrelativistic calculation may likewise be subject to change if relativistic effects are taken into account. Nevertheless, the good agreement between our result for $\delta\langle r^2\rangle$ and the x-ray values in Table VII may be considered as a strong support of the validity of our analysis.

TABLE VII. Change in the mean-square nuclear charge radius for isotope pair ^{178}Hf-^{180}Hf obtained by different experimental methods.

$\delta\langle r^2\rangle$ (fm^2)	Method	Ref.
0.098(13)	optical IS Hf I	This work
0.072(4)	optical IS Hf II	[30]
0.103(7)	electronic x-ray IS	[31]
0.106(7)	muonic x-ray IS	[32]

V. SUMMARY AND CONCLUSION

Hyperfine interaction constants A and B of ^{177}Hf and of ^{179}Hf have been determined for 11 electronic states belonging to the excited configurations $5d^26s6p$ and $5d6s^26p$ and for the $^1D_2$ state of the ground configuration $5d^26s^2$. For the case of the five observed quintet levels of $5d^26s6p$ the A factors could successfully be explained by the three one-electron hfs parameters a_{6s}, a_{6p}, and a_{5d}. A similar treatment of the A factors within the configuration $5d6s^26p$ is complicated by the presence of a considerable amount of configuration mixing and the same holds for the interpretation of the observed B factors. Experimental information on the hfs constants of the complete set of electronic states of these two configurations would certainly represent an improved basis for performing a detailed hfs analysis.

The isotope shifts of the stable Hf isotopes have been obtained for 14 lines in the spectrum of the Hf atom. The effect of SMS and of FS could successfully be separated in Hf for the first time. Relative values of $\delta\langle r^2\rangle$ referred to the isotope pair 178-180 have been deduced for the isotope pairs 174-178, 176-178, 177-178, and 178-179. The FS of the 545.29-nm line has been used to determine an absolute value of $\delta\langle r^2\rangle$ for the isotope pair 178-180. Up to now, the observed electronic factors of the remaining 13 spectral lines have not been analyzed within the present work. Relativistic multiconfiguration Dirac-Fock calculations of the type described in Ref. [28] could be a suitable method of approach for a detailed interpretation of these electronic factors.

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