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Isotope Shift in Hf I*†

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The hyperfine structure in $_{74}$Hf I lines has been resolved and found to consist of either a single line or a well resolved doublet. The components of the doublets are attributed to isotopes 178 and 180. The magnitudes of these shifts have been determined using several independent measurements. The typical size of the doublet separations is about 0.035 K. The arrangement of the shifts indicates that the configuration responsible for seven low-energy levels is $5d^26s^2$. The structure due to isotopes 176, 177, and 179 is nowhere well resolved.

I. INTRODUCTION

Spectroscopic isotope shift at the heavy end of the periodic table is, in the main, the product of the change in the average extension of nuclear charge between isotopes of a given element. The effect has therefore been recognized for some time as a source of information on nuclear properties. Several anomalies, however, appear when the data are compared to the simple volume theory.[1] Perhaps the most troublesome of these is the average smallness[2] of shifts as compared to the values predicted by the theory, taking the nuclear radius to be given by $1.4\times10^{-13}A^{\frac{1}{3}}$. A smaller coefficient in the expression could give agreement, but this possibility was not advanced very firmly for some time. Now, however, recent work on high energy electron scattering and on the gamma-ray spectrum of the μ-mesonic atom points to a nuclear radius substantially smaller than the previously accepted value. This has served to underscore the potential value of isotope shift data.

Isotope shift can further be of assistance in the assignment of terms to electron configurations in the spectrum under examination. Wilets and Bradley emphasize this in their study[3] of isotope shift in Er, where the work was carried out partly to further the analysis of the Er spectra. The latest published analysis[4] of the Hf I spectrum is incomplete and private communication with Meggers revealed that this spectrum has been persistently difficult. Meggers expressed a hope that the data which follow would be of aid.

A survey of the literature showed an obvious gap in knowledge of isotope shift at Hf. Rasmussen[5] reports only on nine lines and, of these, on only two quantitatively. The present work was undertaken, therefore, to extend the data on Hf as far as possible.

II. EXPERIMENTAL

The light source was the standard hollow cathode discharge tube, which was operated at liquid air temperatures. The exposed area of the cathode consisted entirely of Hf. This was machined from a solid cylinder $\frac{1}{4}$ in.$\times\frac{3}{8}$ in. to a taper fit with a copper shell. The sample was 98.98 percent pure and was the very generous donation of the Foote Mineral Company of Berwyn, Pennsylvania. This sample produced a brilliant, clean spectrum for many hundreds of hours of operation.

A quartz Fabry-Perot was the principal instrument of resolution. For this, the flats were kindly loaned by Dean George Harrison of the Massachusetts Institute of Technology. On these, very good Al-Mg surfaces were prepared by O. H. Arroe of the University of Wisconsin; for this generous service the writer is greatly indebted. Six spacers were fabricated from quartz tubing of approximate lengths 2, $2\frac{1}{2}$, 3, $3\frac{1}{2}$, 4, and $4\frac{1}{2}$ cm. Auxiliary dispersion was provided by a large Hilger prism Littrow mounting spectrgoraph. Quartz and glass elements were used to cover the range 2900 to 7000A.

III. RESULTS

The structure consisted of a singlet in 11 lines and of a well resolved doublet on an unresolved background in 63 others. In view of the isotopic composition of natural hafnium, the doublets are expected to correspond to appreciable shifts between isotopes 178 and 180. The isotopic abundances in the naturally occurring material are the following:

Isotope	174	176	177	178	179	180
Abundance (%)	0.18	5.2	18.4	27.1	13.8	35.3

In most cases the relative intensities of components in the doublets made possible simple and unambiguous identification of direction of shift. In a number of lines, however, early examination of structure which had been produced by the lower resolution of smaller spacers revealed relative intensities which appeared to be very nearly equal. Improvement of the resolution later showed the correct directions in these cases and furthermore made it clear that all cases of apparent "negative" direction were in fact all instances of the more common "positive" direction.

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[1] J. H. Bartlett, Nature **128**, 408 (1931); G. Racah, Nature **129**, 723 (1932); J. E. Rosenthal and G. Breit, Phys. Rev. **41**, 459 (1932); G. Breit, Phys. Rev. **42**, 348 (1932).

[2] See, principally, M. F. Crawford and A. L. Schawlow, Phys. Rev. **76**, 1310 (1949); P. Brix and H. Kopfermann, Z. Physik **126**, 344 (1949).

[3] L. Wilets and L. C. Bradley, Phys. Rev. **87**, 1018 (1952).

[4] W. F. Meggers and B. F. Scribner, J. Research Natl. Bur. Standards **4**, 169 (1930).

[5] E. Rasmussen, Naturwiss. **23**, 69 (1935).

When the resolution had been improved enough to show that all resolved shifts were positive, the source of the previous misidentification of direction was fully revealed. Generally in these cases the magnetic splitting of the odd isotopes was sufficiently small that, with relatively poor resolution, the blackening of the plate from the radiation of isotopes 177 and 179 caused the 178 component to appear very definitely more intense. Improved resolution characteristically revealed a pronounced shoulder on the short wavelength side of the true 178 component, and it also reversed the *apparent* relative intensities.

Nowhere was the resolution of the components from isotopes 177 and 179 good enough to permit any conclusions regarding either the character of the possible magnetic splitting or the separation of the center of the 177 "shoulder" from the 178 component.

The magnitudes of the measured shifts between isotopes 178 and 180 are listed in Table I for each line in the Hf I spectrum in which the structure was resolved. An effort was made to obtain values for each shift by using four spacer sizes, but often the exposures with a certain spacer size were not resolved for some line. The number of independent values obtained for any shift is therefore given. The values of shifts listed represent averages of the quantities obtained by using the different spacers. The errors indicate simply the spreads of measured values; a good deal of systematic error from alterations in the pattern caused by the magnetic splitting might not be represented by the errors stated. The lines marked by asterisks were assigned to the Hf I spectrum according to the relative arc and spark intensities given by Meggers,[6] since the lines do not appear in any analysis.

TABLE I. Isotope shifts in Hf I (1 K≡1 kayser≡1 cm^{-1}).[a]

λ(A)[a]	Mean shift, $\Delta\nu_{178-180}$(10^{-3} K)	No. of values	λ(A)[a]	Mean shift, $\Delta\nu_{178-180}$(10^{-3} K)	No. of values
6818.94	Single		3858.30	37.0±1.9	4
6789.27	30.8±1.5	4	3849.17	45.2±1.6	4
6386.23	29.4±1.0	4	3820.74	33.3±0.5	4
6238.58	Single		3811.76	37.9±2.5	4
6098.67	33.2±1.6	4	3800.39	31.1±2.0	2
5902.94	27.1±1.6	4	3785.46*	37.2±2.3	4
5719.18	Single		3777.64	Single	
5613.27	28.5±1.1	4	3733.78	37.5±1.4	4
5552.12	Single		3717.80	39.3±2.4	4
5550.60	27.9±2.4	3	3696.52	32.8±1.6	3
5452.92*	40.2±1.3	3	3682.25	33.2±1.3	3
5438.74	Single		3649.09	39.7±1.9	3
5373.86	29.6±3.0	4	3630.86	23.1±1.2	2
5294.87	27.9±3.1	4	3616.89	33.1±0.9	4
5243.99	42.8±0.8	3	3615.05	37.4±1.6	4
5181.86	22.6±1.4	4	3536.62	35.5±1.9	3
5112.13	42.8±1.5	3	3523.02	31.6±2.0	3
4975.25	37.5±1.1	5	3497.49	33.4±0.6	4
4837.24	23.6±7.0	1	3472.38	28.6±0.8	2
4800.50	Single		3417.35	43.9±1.6	4
4773.72	Single		3332.73	31.6±1.5	3
4655.19	40.1±2.8	4	3312.87	42.4±1.5	4
4620.87*	36.5±4.5	4	3306.12	45.2±0.6	4
4565.94	27.9±1.7	4	3206.11	38.7±1.9	3
4540.92	34.1±1.1	4	3189.63	32.5±3.5	2
4461.17	35.0±4.0	2	3172.94	43.7±3.8	4
4457.35*	37.4±1.3	4	3168.39	Single	
4438.02	38.9±3.2	3	3162.57	39.2±4.0	4
4356.29*	37.0±3.7	4	3156.68	45.8±3.2	4
4294.77	33.7±2.2	4	3131.81	53.4±4.8	4
4228.08	Single		3080.84	41.2±1.0	3
4174.33	29.8±0.7	4	3072.88	37.9±4.4	3
4145.76	36.2±4.9	4	3067.41	35.7±2.2	3
4062.84*	Single		3057.02*	41.5±2.2	4
4032.27	35.5±5.0	3	3050.76	46.3±3.9	4
3951.81	37.3±2.3	4	2964.88	44.6±6.8	2
3899.93	31.0±1.4	4	2950.68	48.5±4.4	3

[a] The lines marked by asterisks were assigned to the Hf I spectrum according to the relative arc and spark intensities given by Meggers (see reference 6).

An examination of the data in terms of the energy level scheme for Hf I is not possible since the analysis for the first Hf spectrum is not complete. It is therefore not possible to calculate the isotope shift constant for Hf nor even to determine the shifts produced in a given term by the presence of a $6s$ electron.

Meggers and Scribner,[4] in their tentative analysis of the Hf I spectrum, give a matrix arrangement which displays the wave number positions of seven low energy levels, the wave number positions of 63 high energy levels and the wave numbers and wavelengths of various transitions between low and high levels. The form is such that any horizontal line across the matrix will select transitions from a single high energy level to the various low levels. Now the electron configurations which can produce the terms evidently responsible for the seven low levels are $5d^26s^2$ and $5d^36s$. And each configuration could produce any or all of these terms, which are ^3F, ^1D, and ^3P. But comparison of these isotope shifts with the matrix shows that without exception the shift is of essentially the same character for every line contained in a single horizontal row. Where the shifts have been resolved, every line in a single row is either single or else every line is double. Hence, a single electron configuration must be responsible for each low energy level, since the configurations have different numbers of $6s$ electrons and would produce different shifts in the low levels. This configuration is, presumably, the $5d^26s^2$ of the ground state.

In the only previous work on the isotope shift in Hf, Rasmussen[5] reported the structure in nine lines. The lines λλ5550, 5452, 5373, 5243, and 4655 were given as double, with the intervals in λλ5550 and 5452 of the respective sizes 0.035 K and 0.043 K. These are somewhat larger than the values obtained here. λλ5613, 5552, 4837, and 4800 were all reported as single, while λ5613 and λ4837 here very definitely appeared double. Rasmussen states that, on the basis of the observed number of components apparently produced by magnetic splitting of the odd isotopes, the spins of both the 177 nucleus and the 179 nucleus are probably either $\frac{1}{2}$ or

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[6] W. F. Meggers, J. Research Natl. Bur. Standards 1, 151 (1928).

$\frac{3}{2}$. It is impossible to confirm this from the structure observed in any line.

Further work is being done on samples enriched in the isotopes 174 and 176 in order to determine the shifts 174–176 and 176–178. The interference systems on hand at this writing do not warrant even qualitative conclusions, however.

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Electronic Polarizabilities of Ions from the Hartree-Fock Wave Functions*†

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The electronic polarizability α has been calculated for several ions by obtaining the perturbation of the wave functions by an external field from a numerical solution of the differential equation satisfied by the perturbation. For the helium-like ions an analytic solution was obtained by using the wave functions of Löwdin. The calculated values of α are, in general, between 1 and 1.5 times the observed values. For several ions values have been calculated for the quadrupole polarizability which measures the quadrupole moment induced in the ion by an external charge. The effect of the dipole moment induced in the ion on the electric field at the nucleus is discussed.

I. INTRODUCTION

THE electronic polarizability of ions has been determined by a number of different methods. The polarizability can be obtained from the index of refraction of the ion in solutions or in crystals. An independent method consists in a consideration of the Rydberg-Ritz correction for the spectral series of atoms. Following Born and Heisenberg,[1] the deviation of the spectral terms of the alkalis from hydrogenic levels is attributed to the polarization of the core by the valence electron. This procedure to obtain the polarizability was also used by Mayer and Mayer.[2] The determination of the polarizability from the index of refraction of solutions was first carried out by Heydweiller[3] and by Fajans and Joos.[4] While the present work was in progress, there appeared a paper by Tessman, Kahn, and Shockley[5] who made a determination of the ionic polarizabilities from the experimental refraction data of crystals containing the ions considered.[6]

In contrast to the variety of experimental determinations of the polarizability α, there exist comparatively few theoretical treatments which attempt to explain the values of α in terms of the electronic structure of the ion. Pauling[7] derived an analytic expression for α for electrons which move in a pure Coulomb field (hydrogenic wave functions). He used this expression with appropriate screening constants for the helium-like ions and obtained good agreement with the observed values of α. This method is not expected to give accurate results for medium and heavy ions since the electronic wave functions are very different from hydrogenic wave functions in this case. Buckingham[8] obtained an expression relating α to the average values of r^2 for the various electron shells, where r is the distance between the nucleus and an electron of the core. This expression was derived from a variational calculation in which the perturbed wave function for each shell was taken as a preassigned function times a parameter which was varied to minimize the energy. Although different parameters were used for the different subshells, this procedure probably does not always give a good approximation to the actual perturbed function, because only a single parameter for each subshell is available in the variational calculation.

In the present paper, values of α are obtained for nine ions from F^- to Cs^+ by means of a numerical solution of the differential equation for the perturbation of the electronic wave functions for the various shells. For the unperturbed wave functions, the Hartree-Fock functions of the ions are used. For the helium-like ions an approximate analytic solution for the perturbation based on the wave functions of Löwdin[9] will be employed. The calculated values of α lie, in general, between 1 and 1.5 times the experimental values. Thus the calculations are in reasonable agreement with ex-

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† A preliminary account of this work was presented at the April 29–May 1, 1954 Meeting of the American Physical Society in Washington, D. C. [Phys. Rev. 95, 594 (1954)].

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[2] J. E. Mayer and M. G. Mayer, Phys. Rev. 43, 605 (1933).

[3] A. Heydweiller, Physik. Z. 26, 526 (1925).

[4] K. Fajans and G. Joos, Z. Physik. 23, 1 (1924).

[5] Tessman, Kahn, and Shockley, Phys. Rev. 92, 890 (1953).

[6] An extensive discussion of the work on polarizabilities is given by J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), first edition, Chap. VIII.

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[8] R. A. Buckingham, Proc. Roy. Soc. (London) **A160**, 94 (1935).

[9] P. O. Löwdin, Phys. Rev. **90**, 120 (1953).