PHYSICAL REVIEW A **70**, 032506 (2004)

Wavelengths of the $4s_{1/2}$-$4p_{3/2}$ resonance lines in Cu- and Zn-like heavy ions

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(Received 9 March 2004; published 21 September 2004)

The euv resonance lines $4s_{1/2}$-$4p_{3/2}$ of the Cu- and Zn-like ions of Os, Bi, Th, and U $(Z=76-92)$ have been observed in an electron beam ion trap, and their wavelengths measured using a high-resolution flat-field spectrometer. Our experiments achieve a spectral resolution three to six times better than earlier measurements and remove potential systematic errors from line blends encountered in earlier work. Our results for Cu-like ions are in good agreement only with recent *ab initio* calculations that include quantum electrodynamical effects. Our experimental results for Zn-like ions have a similarly high accuracy. However, theoretical predictions for Zn-like ions of a quality comparable to those available for Cu-like ions are lacking.

DOI: 10.1103/PhysRevA.70.032506 PACS number(s): 32.30.Jc, 34.50.Fa, 34.80.Dp

I. INTRODUCTION

The study of ions along the Cu isoelectronic sequence provides important benchmarks through both precision experiments and modern atomic structure theory. Production and charge-state isolation are more easily achieved for Cu-like ions than for ions of many other charge states. Plasmas produced by some of the most powerful laser systems, such as the NOVA and OMEGA lasers, have been sufficient to reach Cu-like ions of the heaviest naturally occurring elements years ago. However, the laser-produced plasma data in the high-nuclear charge (high-Z) regime [1] deviate from calculation (for example, that by Kim *et al.* [2]) by several hundred ppm for the heaviest elements. Lower-Z ions measured in lower-density tokamaks do not exhibit any noticeable difference with theory. In a recent paper [3], we have presented data from observations of high-Z $4s_{1/2}$-$4p_{3/2}$ lines in the low-density environment of the EBIT-II electron beam ion trap. Our measurements continued the good agreement with theory established by the tokamak data and disagreed with the high-Z trend set by the laser-produced plasma measurements. However, a small deviation between the EBIT-II data and theory by Kim *et al.* was found for the two highest-Z ions, Th^{61+} and U^{63+}. Here, the measured wavelengths were slightly longer than predicted by the calculations by Kim *et al.* [2]. The data point for Th^{61+} agreed with the trend of the *ab initio* calculation by Blundell [4], but the data point for U^{63+} did not. Since then, theory has been checked by new high-precision calculations of relativistic correlation energies and QED corrections [5]. The latest calculations confirm the trend of Blundell's calculations, but could not provide better agreement with experiment for U^{63+}.

In the following we present a greatly improved experimental study of the $4s_{1/2}$-$4p_{3/2}$ transition energies of high-Z Cu-like ions. We have used the EBIT-I electron beam ion trap. The major improvement lies in the implementation of a new spectrometer that affords a three- to sixfold increase in spectral resolution over the spectrometer used on the EBIT-II electron beam ion trap. This is now by far the grating spectrometer with the highest resolving power in this extreme ultraviolet to soft-x-ray spectral range, at any electron beam ion trap. The notably improved spectral resolution allows us to account for potential shifts of the apparent line positions. Overall we achieve a factor of 3 higher accuracy in our measurements, providing an accuracy within 35 ppm. The new measurements thus are the most accurate from such highly charged ions in this spectral region. (Only a single-element observation, of the Na-like ion U^{81+}, with a crystal spectrometer, has reached an even more accurate result (16 ppm) in this range before [6].) The data presented here are the first to discriminate between the best calculations of Cu-like ions, agreeing with the calculations by Blundell. The earlier disagreement between theory and experiment for U^{63+} is removed by our new measurements, indicating a flaw with the EBIT-II results.

The $4s_{1/2}$-$4p_{3/2}$ resonance line ($4s^2\ {}^1S_0$-$4s4p\ {}^1P_1^o$ in *LS* coupling notation) of the Zn-like ions appears alongside the aforementioned transition in the Cu-like ions. Consequently, our measurements provide equally precise wavelength data for this transition in the Zn-like ions as for the Cu isoelectronic sequence. Theory, however, faces the problem of treating an additional electron in the valence shell. As demonstrated elsewhere [7], various calculations have been tried to this effect, but none has reached satisfactory results. In fact, theory is poorer in the prediction of levels in Zn-like ions than in Cu-like ions by more than a factor of 100. As the QED corrections are expected to be rather similar in both atomic systems (and have been tested by our measurements on Cu-like ions), the calculational obstacles must relate to the non-QED part of the problem, most likely to the interaction of electrons in the valence shell. We provide alternative, highly accurate data on the $4s_{1/2}$-$4p_{3/2}$ transition in Zn-like ions as benchmarks in the quest for a satisfactory description of electron-electron interaction in systems with two valence electrons.

II. EXPERIMENT

The experiment was done at the University of California Lawrence Livermore National Laboratory electron beam ion trap facility. Of the laboratory's two electron beam ion traps, the higher-energy device, SuperEBIT [8], as well as its low-energy configuration, EBIT-I, were employed. Much of the

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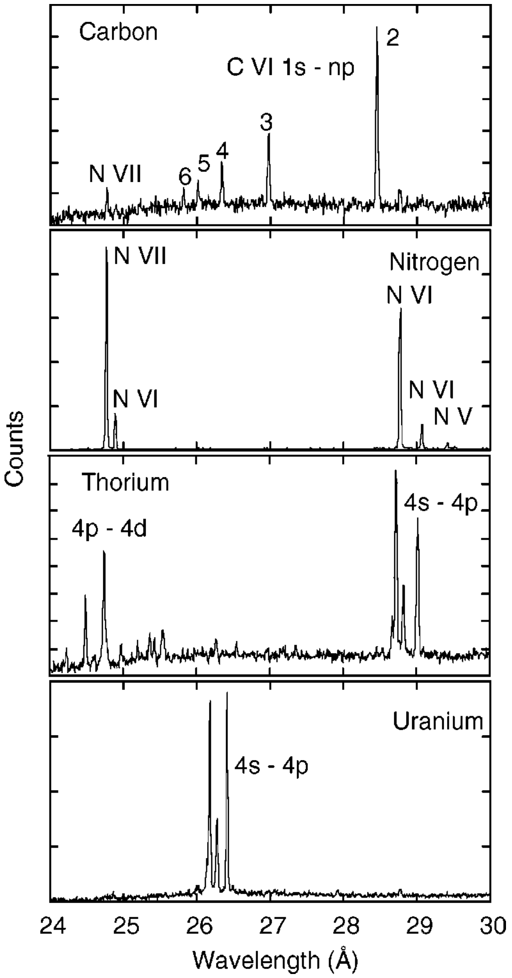

FIG. 1. Spectra with nitrogen, carbon dioxide, thorium, or uranium injection into the electron beam ion trap. Both heavy-element spectra are calibrated by observations of lines from H- and He-like light ions.

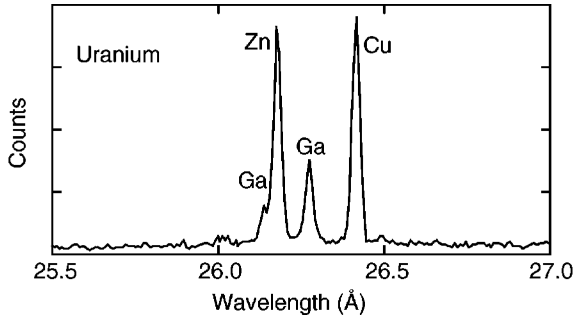

FIG. 2. Detail of an euv spectrum obtained with uranium injection (see Fig. 1). The spectral lines originate from Cu-like, Zn-like, and Ga-like ions of uranium.

experimental procedure has been explained before [3,7] and does not need to be repeated here. The new measurements covered the elements Os (Z=76), Bi (Z=83), Th (Z=90), and U (Z=92). Ions of Bi, Th, and U, respectively, were introduced into the electron beam ion trap by means of a metal vapor vacuum arc ion source; for Os, a volatile compound, osmium tetroxide, was used by ways of a low-pressure, ballistic gas injector, instead. Upon breaking the molecule by collisions with the fast electrons of the beam, the light ion radicals evaporate from the trap volume and provide evaporative cooling to the Os ion cloud. For easier trapping of the other elements, nitrogen (in some cases carbon dioxide) was bled into the vacuum vessel via the ballistic gas injector. Ions were trapped by the combination of a strong (3 T) magnetic field for radial confinement, electric fields in a drift tube arrangement for axial confinement, and the attractive potential offered by the intense electron beam.

Bombarded by the electron beam, the ions are being ionized in a stepwise fashion. Ionization ends when the charge state reached has a higher ionization energy than is available as kinetic energy in the electron beam. The electron beam energy necessary to create Cu-like ions is of the order 2.0–4.5 keV for the elements considered here [10], which is but a small fraction of the working range of SuperEBIT. The ionization energy of the next higher charge state, Ni-like ions, is relatively high (and the prominent lines lie in other ranges of the spectrum). Consequently, a wide range of electron beam energies is available to create a charge state balance that is dominated by Cu- and Ni-like ions, by burning out the lower charge states, and thus creating "clean" euv spectra with mostly lines from Cu-like and Zn-like ions re-

TABLE I. Predicted and measured wavelengths (in angstroms) of the $4s\ ^2S_{1/2}$-$4p\ ^2P^o_{3/2}$ transition in Cu-like ions of the eight highest-Z ions covered in these experiments. Of the earlier experimental results, only a representative one of the laser-produced plasma studies is quoted.

Element	Z	Semiempirical [1]	Theory [2]	Theory [4]	Experiment [1]	Experiment [3]	Experiment this work
Yb	70	75.839	75.860	75.864	75.842(15)	75.8595(47)	
W	74	62.311	62.334	62.341	62.304(15)	62.3355(45)	
Os	76	56.534	56.558				56.5630(20)
Au	79	48.907	48.931		48.928(15)	48.9280(26)	
Pb	82	42.358	42.377	42.381	42.349(15)	42.3740(58)	
Bi	83	40.383	40.404	40.407	40.394(15)		40.4066(20)
Th	90	28.998	29.018	29.022	28.990(15)	29.0224(30)	29.0227(10)
U	92	26.401	26.420	26.423	26.400(15)	26.4325(19)	26.4233(15)

TABLE II. Predicted and measured wavelengths of the $4s^2\ {}^1S_0$-$4s4p\ {}^1P_1^o$ transition in Zn-like ions. All wavelength values are given in angstroms.

Element	Z	Theory	Experiment i[f]	Experiment[g]	Experiment[h]
Yb	70	73.430[a] 73.8[b] 73.368[c] 73.784[d]	73.792(20)	73.8070(66)	
W	74	60.629[a] 61.0[b] 60.585[c] 60.907[d] 60.806[e]	60.900(20)	60.9300(54)	
Os	76	55.4[b] 55.084[c] 55.373[d]			55.3840(50)
Au	79	48.0[b] 47.787[c] 48.038[d] 47.7[e] 47.991[e]	48.063(20)	48.0583(49)	
Pb	82	41.7[b] 41.483[c] 41.708[d] 41.681[e]	41.689(20)	41.7185(45)	
Bi	83	39.8[b] 39.578[c] 39.796[d]	39.792(20)		39.8151(20)
Th	90	28.6[b] 28.52[c] 28.704[d] 28.707[e]	28.702(20)	28.7227(67)	28.7303(11)
U	92	26.1[b] 25.975[c] 26.152[d] 26.168[e]	26.157(20)	26.1868(36)	26.1861(10)

[a] Multiconfiguration Dirac-Fock (MCDF) [22].
[b] Semiempirical analysis of experimental data [23].
[c] HULLAC [19].
[d] HULLAC plus semiempirical correction [19].
[e] Multiconfiguration Dirac-Fock (MCDF), with QED, including nuclear size effects [21].
[f] Reference [19].
[g] Reference [7].
[h] This work.

maining. On the other hand, electron beam energies below the production threshold of these two ion species were employed to learn about possible contamination of the spectra by lines from ions in lower charge states.

The present measurements employed a new flat-field spectrometer system (FFS) [9] that represents an improvement in spectral resolution by a factor of 3 to 6 over our previous instrument. The spectrometer is equipped with a 2400 ℓ/mm variable line spaced concave grating of $R = 44.3$ m radius of curvature and with one of two cryogenically cooled back-thinned charge-coupled device (CCD) cameras. The older of the two CCD cameras contains a chip that has 1024×1024 pixels on a square area of about 25 mm edge length. The newer camera has 1340×1300 pixels on about the same area. The grating imaged the light from the ion trap, using the 60 μm diameter electron beam [11] as the source, onto the CCD chip where it resulted in the geometrically expected width of about 3 to 4 pixels (older CCD) to 4 to 5 pixels (newer CCD), respectively.

With the older CCD camera, the total area of the CCD chip was binned by a factor of 4 in the nondispersive direction to create an effective CCD array of 256×1024 pixels. Due to spectral aberrations, the image of each line is slightly curved at the CCD surface. Simple summing across the dis-

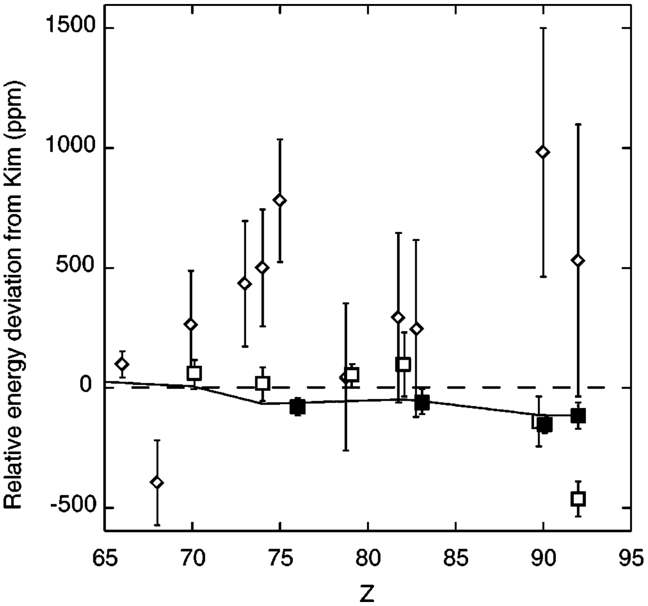

FIG. 3. Relative deviation of predictions and data for the $4p\ ^2P^o_{3/2}$ level energy in Cu-like ions from the values predicted by Kim *et al.* [2] (dashed line at zero). Full line, [4]; diamond, data from sources other than the electron beam ion trap; open squares, [3], solid squares: this work.

persion direction would, therefore, result in spectral features broadened to about five channels. As the signal level was quite high, we elected to evaluate only the center part of the spectra where the line curvature is less of a problem. Spectra were recorded of Os, Th, and U, with typical exposure times of 20 min per spectrum. Calibrations were done before and after some 4 to 6 h of data taking.

With the newer CCD, the spectral image area was subdivided into three parallel strips along the direction of dispersion. The spectra of each strip were separately calibrated and evaluated, resulting in 48 individual measurements for Bi, 24 for Th, and 30 for U. The 30-min exposures were interspersed with calibration spectra every hour or two. Moreover, in several spectra of Bi and Th, the calibration was affected in the very spectra, by increasing the amount of cooling gas until the lines of the light elements appeared along the ones of the heavy element.

Calibration was performed by reference to a number of well known transitions in H- and He-like ions of C, N, and O (mostly from separate exposures, using CO_2 or N_2 gas injection and short timing cycles), then fitting a second-order polynomial to the calibration data. For reference line wavelengths, we used the calculations by Garcia and Mack for H-like ions [12] and those by Drake for $n=2$ levels of He-like ions [13]. For both sets of calculations, the accuracy is assumed to be better than 1 mÅ. For some singlet lines in He-like ions of N and O, Engström and Litzén [14] provide even more accurate reference wavelengths, and they correct significant errors in the Kelly tables [15].

The lines of interest in Bi and Th lie very close to the strong lines that result from $1s^2$-$1s2p$ transitions in He-like carbon and nitrogen, respectively, which renders the best situation for the calibration effort. Examples of the heavy-ion spectra and light-ion calibration spectra are shown in Fig. 1.

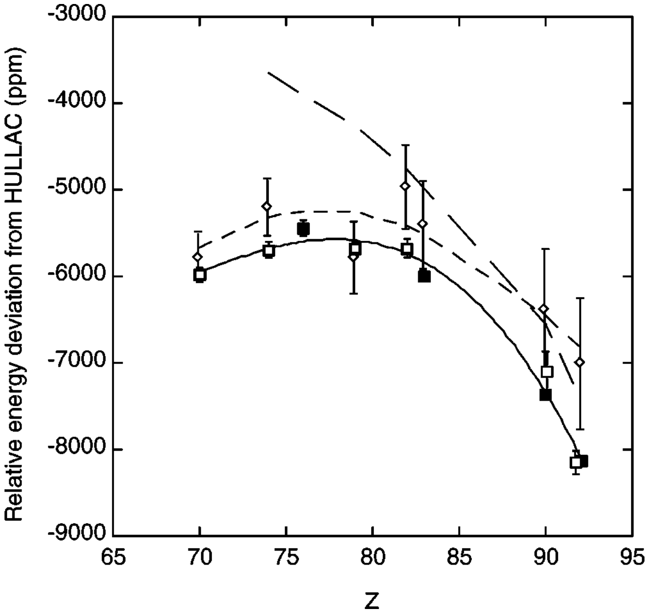

FIG. 4. Relative deviation of predictions and experimental data for the $4s^2\ ^1S_0$-$4s4p\ ^1P^o_1$ transition energy in Zn-like ions from the values predicted by Brown *et al.* [19] using the HULLAC [24] code. Theory: long dashed line: HULLAC plus semiempirical correction: [19], short dashed line: [21], experiment: open circles: [19], open squares: [7], solid squares: this work. On this scale, the error bars for some of the new data are smaller than the symbol size. The solid line provides a (third order polynomial fit) guide to the eye for the electron beam ion trap data.

The lines of H-like and He-like N were used in [3] for the calibration of the U lines. However, these are relatively far apart and the U lines are situated well in between. Therefore, these lines provide a reference wavelength scale that is less accurate than in the case of the Th lines, which are almost coincident with the K-shell lines of He-like N (see Fig. 1). Because of this situation, we employed an additional set of reference lines given by the $1s$-np Lyman series of H-like C. The series limit of $1s$-np transitions in H-like ions of carbon is near the U lines of present interest. These calibration lines are well known, but weak. By their multitude they nevertheless provide a reliable reference grid. For Os, second diffraction order lines of nitrogen were used that were not so close in position and not so tightly spaced as in the other cases, thus affording a somewhat lower calibration precision.

Both CCD chips have different background distributions, but none had any prominent features that would perturb the determination of line positions. Therefore a flat background (representing most of the read-out noise) was subtracted from the raw data before evaluation, and the rest was approximated by a low-order polynomial function. The peaks were fit with Gaussian functions.

The line width of such a grating spectrometer as that employed here is largely given by the source width and thus practically constant over the working range. The resolving power $\lambda/\Delta\lambda$ consequently is lowest at the shortest wavelengths covered. We therefore demonstrate our improvement in resolution with data for uranium (Fig. 2) which represent the lower limit of the resolution achieved. Clearly the profile of the line labeled "Zn" has some overlap with a weaker line of other origin, but the wavelength difference is large enough to permit a reliable multi-peak fit analysis. The line structure is basically similar in all ions studied here.

While the blending problem has been largely overcome with the new instrument, the remaining principal sources of error are signal statistics and measurement reproducibility. By straightforward statistical analysis, the positions of the lines of interest can be determined to about 10% of the line width. However, the distribution of results from many repeat measurements was not Gaussian. We therefore quote an error margin that encompasses two-thirds of all data points, and this amounts to 1 to 2 mÅ.

III. RESULTS AND DISCUSSION

A summary of the results from each of the measurements of Cu-like ions is found in Table I. Results on Zn-like ions are listed in Table II. In both cases we also list some selected theory values, leaving out most of those shown previously to be less satisfactory. We also list the earlier EBIT-II results, as well as representative data from other experiments [1,16–19]. The much better spectral resolution of the present work practically removes line blends as a significant source of systematic error. The present results agree in many cases with the EBIT-II data within the respective error bars. However, there is a slight shift away from the EBIT-II results, which makes for excellent overall agreement with the prediction by Blundell [4] while no longer overlapping with the prediction by Kim *et al.* [2] in the case of the heaviest Cu-like ions, as shown in Fig. 3. Our data point for U^{63+} disagrees strongly with the calculation by Kim *et al.*, but is in excellent agreement with the prediction by Blundell.

Concerning Zn-like ions, the disagreement between theoretical predictions and experimental findings is considerable, as is illustrated in Fig. 4. The figure includes only the most accurate theoretical results we are aware of; we note that the offset from *ab initio* calculational results is about 5000 ppm. This is about two orders of magnitude more than is seen in the Cu isoelectronic sequence. Clearly, electron-electron interactions in ions with more than one electron in the valence shell deserve more theoretical attention, now that experimental benchmark data are available. Until such calculations are made, we note that the semi-empirical predictions [19,21] also are in need of revision. The better of the two will need to be shifted by about 300 ppm in the range $70 \leqslant Z \leqslant 85$ and by more than 1000 ppm for uranium.

On a final note, we point out that the present results bode well for future measurements of the $3s_{1/2}$-$3p_{1/2}$ and $2s_{1/2}$-$2p_{1/2}$ valence transitions in very high-Z Na-like and Li-like ions, respectively, which also fall into the wavelength region spanned by the present measurements. Recent measurements of xenon with a lower-resolution instrument have shown the feasibility of such experiments on SuperEBIT [20].

ACKNOWLEDGMENTS

We are happy to acknowledge the dedicated technical support by Ed Magee, Merv Lawrence, and Phil D'Antonio. E.T. gratefully acknowledges travel support by the German Research Association (DFG). The work at the University of California Lawrence Livermore National Laboratory was performed under the auspices of the U.S. Department of Energy under Contract No. W-7405-Eng-48.

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