Wavelength measurement of the prominent *M*1 transition in the ground state of Ti-like Pt, Au, and Tl ions

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Using a high-efficiency, transmission grating spectrometer at an electron-beam ion trap, the $3s^2 3p^6 3d^4\ J=2-3$ transition in the ground configuration of the Ti-like ions Pt^{56+}, Au^{57+}, and Tl^{59+} was measured. The measurements achieved up to 20 times better precision than previously reported other high-Z measurements.

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I. INTRODUCTION

Accurate measurements of transition energies within the ground configuration of highly charged ions serve as benchmarks for the accuracy of atomic structure calculations. Electric-dipole forbidden transitions between such levels are variously employed for the diagnostics of terrestrial and astrophysical plasmas. As plasma devices achieve progressively higher temperatures, a particular interest arises for such transitions in high-Z ions, preferentially with ionization potentials between 5 and 10 keV. Feldman, Indelicato, and Sugar carried out a broad range theoretical survey [1] and identified a particular case that since has found great interest theoretically and experimentally. In ions with a $3s^2 3p^6 3d^l$ ground configuration a peculiarity occurs, which is a transition that is almost constant in transition energy for a fairly wide range of nuclear charges, from Z=60 to Z=92. Feldman *et al.* predicted that the fine structure transition $3s^2 3p^6 3d^4\ J=2-3$ within the ground configuration of these Ti-like ions has a wavelength of $\lambda_{Nd}=3557$ Å at $Z=60$, changes very little to $\lambda_W=3546$ Å at $Z=74$, and slowly declines in wavelength to $\lambda_U=3200$ Å at $Z=92$. The calculations of this 22-electron system were done not fully *ab initio*, but implied a rough scaling of certain parameters based on general experiences with such calculations.

Soon after, the first measurements of this transition in Xe^{32+} and Ba^{34+} [2], using an electron-beam ion trap at NIST Gaithersburg, identified the lines, but reported results that differed from the calculations by about 200 Å. Within a few years, further results for a fair number of ions were obtained at the electron-beam ion traps at Livermore [3,4], Oxford [5,6], Tokyo [7–11], and again Gaithersburg [12]. The latest systematic analysis [13] lists data for 18 elements.

Because of the promising plasma physical application on one hand and the imprecise initial prediction on the other, various attempts were made to improve on the theoretical treatment of these transitions, including semiempirical scaling attempts [14], *ab initio* calculations [8–10,15–18], and full-scale calculations with semiempirical parameter fitting [13]. Although clearly much progress has been made, at least two areas of problems remain. One is a puzzling irregularity of certain atomic parameters near $Z=53$, which appears in both the multiconfiguration Dirac-Fock (MCDF) calculations by Kato and co-workers [8–10] and in the Hartree-Fock relativistic (HFR) calculations by Biémont *et al.* [13]. The other is the situation at high nuclear charges where so far only a single precise data point (for $Z=74$) [4] is available. Since relativistic calculations converge better for high ion charges than for low ones, it deemed sensible to provide more precise experimental data in that range. We therefore extended our study on W to Pt ($Z=78$), Au ($Z=79$), and Tl ($Z=81$), facing the problem that the transition of interest becomes the progressively weaker decay branch of the upper level. For W^{52+}, only 16% of the $J=3$ population is expected to go to the $J=2$ level, and for U^{70+} this fraction drops to only 5% [1]. The percentages differ between the various calculations, but the general trend is being predicted similarly by all.

II. EXPERIMENTAL SETUP AND MEASUREMENT

The measurement was performed at the EBIT-II facility at the Lawrence Livermore National Laboratory, one of the two original electron-beam ion traps [19]. In order to make precision measurements on high-Z elements, it is necessary to achieve both high spectral resolution and high-efficiency optical detection. We used a newly developed transmission grating spectrometer consisting of a matched pair of $f/4.6$ achromatic lenses, a high-efficiency, 15-cm-diameter planar quartz transmission grating, and a back-thinned, cryogenically-cooled charge-coupled device detector [20]. Using two identical lenses and no external slit, a one-to-one image of the photon emitting ions within the electron-beam ion trap is projected onto the two-dimensional detector plane. Slitless operation is possible because in EBIT-II, the ions emit only in a narrow region defined by the 50-μm-diameter electron beam [19].

For setting up the spectrometer, we took guidance from the calculations by Feldman *et al.* and from their mismatch with experimental findings at lower-Z elements. Meanwhile, several calculations [9,10,13] yield a more reliable guidance for some elements, to within better than 3 Å, or about 0.1% of the wavelength. The spectrometer was calibrated *in situ*, using the ''inverted trap'' technique explained earlier [4]. In this technique, the drift tube voltages are set in a way not to trap, but to expel ions. Ne or Kr atoms injected by the gas injector and streaming through the chamber then cross the electron beam with a good chance of being excited or ion-

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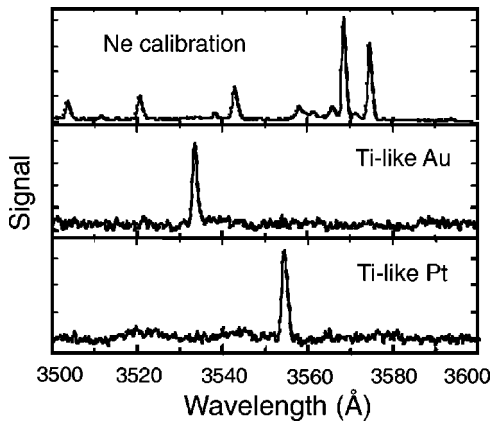

FIG. 1. *In situ* calibration spectrum showing lines from low-charge states of neon and two spectra of Pt and Au, each with the prominent (and only) line of interest from the Ti-like ion.

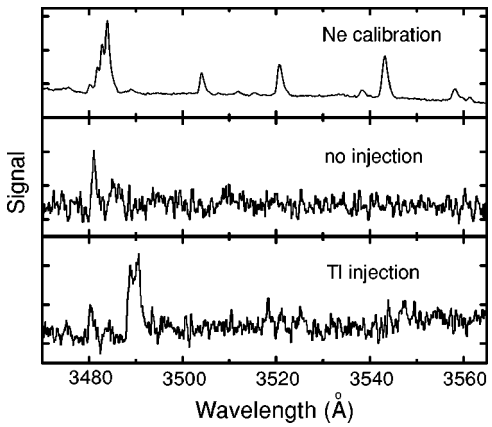

FIG. 2. Spectra from one setting of the transmission grating spectrometer. Top, calibration spectrum of Ne, obtained with an inverted trap; middle, observation without any ion injection; bottom, with Tl ion injection, a double line appears, consisting of the candidate line from the Ti-like ion Tl^{59+} and an unidentified corresponding line from another charge state Tl ion (see text).

ized, but only once or very few times. Prompt emission shows a spectrum that is dominated by lines belonging to singly charged ions, with a sufficient number of well-known lines among them. The geometry of observation is the very same as with trapped ions, and there is no need for extra optics etc. Figure 1 shows a calibration spectrum and spectra obtained with trapped Pt and Au ions for comparison.

The electron-beam energy necessary to create the Ti-like charge state—22 remaining bound electrons—is 4.72 keV for W^{52+} (we include the previously published experiment on W in the discussion, because it is an anchor for these measurements), 5.42 keV for Pt^{56+}, 5.61 keV for Au^{57+}, and 5.98 keV for Tl^{59+} [21]. When searching for the respective line in a new ion species, the electron-beam energy was set about 150 eV above production threshold. At these energies, typical electron-beam currents ran near $I_{beam}=130$ mA. The detector accumulated signal for 20 min for each spectrum, covering about 130 Å at a time. The detector was then shifted and a new spectrum recorded, covering a total range of about 500 Å for each element. Usually, only a single spectral line was detected for each species. In order to ascertain the emitting charge state, the electron-beam energy was then varied from below threshold to values well above. A typical excitation curve thus obtained has been shown previously [4]. The combination of wavelength (by comparison to theory-guided expectation) and production threshold (charge state assignment via the ionization potential of the next lower charge state ion) was taken as proof of identity with the desired $J=2$-3 transition in the Ti-like ion.

The electron-beam energy was then adjusted until an optimal count rate was achieved in the line. Data were accumulated for many hours, alternating the specific ion injection with either the Ne or Kr gas injection. Multiple measurements of the transition with various electron-beam currents and energies were made for each of the lines, accumulating a statistically significant number of counts. The scatter of the various measurements was about ten times larger than the statistical uncertainty of the individual measurements, some 18 μm, or about 0.10 Å on the calibrated wavelength scale. Systematic studies of the stability of the electron beam revealed no measurable shift in the electron-beam position during steady-state operation [22]. A slight movement of the spectrometer system was tracked down to temperature fluctuations in the laboratory. These may well account for most of the measured scatter of the line positions noted in the analysis, and they presently limit the precision of our measurements. The majority of the calibration lines are known to better than 0.01 Å [23] and, therefore, add no significant adjustments to the error budget. The final result of our measurement is 3627.13 ± 0.10 Å for W, 3554.46 ± 0.10 Å for Pt, 3533.53 ± 0.10 Å for Au, and about 3490 Å for Tl.

For the latter element there is a problem, inasmuch as the line profile (Fig. 2) consists of two components (at 3488.94 Å and 3490.61 Å , respectively; line width 1.60 Å) that differ in wavelength by about 1.7 Å. The question arises whether this structure reflects nuclear effects in the Ti-like ion (isotopes 203 and 205 are the most abundant), or whether the two lines represent electric-dipole forbidden transitions in different ions of Tl [24]. The latter assumption appears more likely, considering that in comparable electron-beam ion trap spectra of several other elements such chance coincidences have been seen [10,14], although in none of those spectra the proximity was as close as in the present case. Hartree-Fock calculations with relativistic corrections were therefore performed by Biémont [25], using typical scaling parameters for lack of any spectroscopic data, and they indicate candidate lines in various near-by charge states. The expected closest match would be with a line $(3d^3\,{}^4P^o_{3/2}\text{-}{}^2P^o_{1/2})$ in the Sc-like ion Tl^{60+}, with a wavelength prediction about 26 Å below that for the Ti-like ion. In the V-like ion Tl^{58+}, a candidate line $(3d^5\,{}^4D^o_{7/2}\text{-}{}^4G^o_{9/2})$ would be expected about 80 Å below our reference, and in Mn-like Tl^{56+} at 120 Å above. Given the problem of calculating such fine-structure transitions to better than 10%, none of these can be ruled out on the basis of their predicted wavelengths. The ionization potentials of all these ions are so close to each other that no experimental discrimination by way of electron energy variation would be

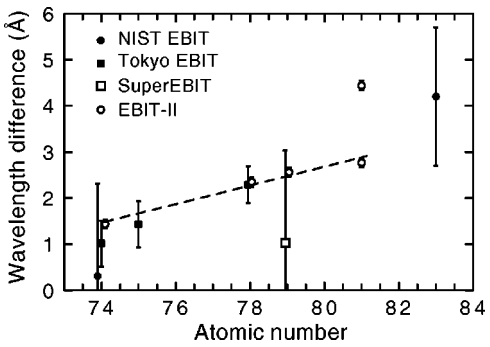

FIG. 3. Difference of experimental and theoretical [9] wavelength data in the high-Z range of Ti-like ions. The data can be identified from Table I. An eye-guiding dashed line connects our own results and suggests a linear term for the mismatch between these data and the predictions by Kato *et al.* [9]. Note that the error bars of our data barely exceed the symbol size.

decisive either. No further line was seen in a 500-Å range near to the line of interest. Last, but not the least, the two candidate lines are so close to each other in wavelength that it is not evident which one actually is the sought-after line in the Ti-like ion. Comparing the experimental results for various ions to the predictions by the three most successful calculations [9,10,13] yields no obvious answer either, since the high-Z trends of the calculations differ and the experimental data are sparse. The shorter-wavelength component of the line pair (3488.94 Å) would perhaps fit best, with a 3-Å deviation from the Japanese calculations in a range where their mismatch with theory increases from 2 Å (near $Z=72$) to 5 Å (near $Z=83$). Figure 3 shows the situation and suggests a best data trend that is represented by a linear offset from the calculations by Kato *et al.* The puzzle can only be solved by high-precision measurements on further high-Z ions in the vicinity of $Z=82$, exploiting the different Z scaling of $M1$ transitions in different ions.

III. DISCUSSION

In Table I, we list several predictions and all available data of this unique transition for the Ti-like ion species from $Z=70$ through $Z=83$ (plus $Z=92$). This range includes all elements that are covered in our study. One inconsistency perveates all these comparisons: the calculational results usually refer to level energy differences and thus to transition wavelengths in vacuum. The measurements of wavelengths in these ions, however, are all done in air (though, at the

TABLE I. Predicted and measured values for the wavelengths of the $3s^2 3p^6 3d^4$ $J=2-3$ transition along the Ti isoelectronic sequence. It is customary to quote wavelengths above 2000 Å as air wavelengths. However, not all of the reference data listed are specified for vacuum or air wavelength. We therefore quote the values as given in the references.

		Predicted wavelength (Å)						Measured (air)
Element	Z	Feldman [a]	Serpa [b]	Kato [c]	Watanabe [d]	Biémont [e]	Froese Fischer [f]	Wavelength (Å)
Yb	70	3564.5		3676.71	3675.7	3674.4	3655.4	3676.4(1.5) [g]
Lu	71			3666.32		3666.2		
Hf	72		3562	3654.34	3653.3	3655.6		3655.4(0.4) [d]
Ta	73			3640.77	3639.7	3641.8		3641.8(0.5) [d]
W	74	3546.1	3524	3625.69	3624.7	3627.2	3606.8	3626(2) [g]
								3627.13(0.10) [h]
								3626.7(0.5) [d]
Re	75			3609.17	3608.1	3610.7		3610.6(0.5) [d]
Os	76		3507	3591.33		3593.0		
Ir	77			3572.27		3574.6		
Pt	78			3552.11	3551.1	3554.4		3554.4(0.4) [d]
								3554.46(0.10) [h]
Au	79			3530.97	3530.0	3532.1	3515.4	3532(2) [i]
								3533.53(0.10) [h]
Hg	80			3508.96		3507.0		
Tl	81			3486.17		3482.0		3488.94(0.10) [h]
								3490.61(0.10) [h j]
Pb	82	3427.3		3462.72		3453.5		
Bi	83	3442 [k]		3438.70	3437.7	3423.0	3425.8	3442.9(1.5) [g]
U	92	3199.7		3209.0				

[a] Feldman *et al.* [1].
[b] Serpa *et al.* [14].
[c] Kato *et al.* [9].
[d] Watanabe *et al.* [10].
[e] Biémont *et al.* [13].
[f] Froese Fischer and Fritzsche [18].
[g] Porto *et al.* [12].
[h] Present work, including Utter *et al.* [4].
[i] Träbert *et al.* [3].
[j] Alternate line identification.
[k] Beck [17].

present level of precision, without monitoring the various parameters such as pressure, temperature, and CO_2 concentration, which are required for a reliable conversion to vacuum wavelengths). They refer to reference wavelengths that are also given in air, as is customary for wavelength above 2000 Å. A correction of our results to vacuum wavelengths would result in wavelength values that are typically longer than the air wavelengths by about 1.00 Å. Since most calculations predict wavelengths that are shorter than the ones actually measured, this would increase the discrepancy.

Evidently, the early calculations by Feldman *et al.* [1] have served their purpose in showing the way, but at deviations of order 200 Å between experiment and calculation, they are rather inaccurate. A semiempirical analysis and extrapolation towards higher charges by Serpa *et al.* [14] turned out worse than the aforementioned calculation in the high-*Z* range. Next, Beck [16,17] provided dedicated calculations for a few selected ions. These isolated results, unfortunately, do not have much predictive power for elements not yet handled. The first set of *ab initio* calculations that yielded wide-range predictions that also came close to the experimental findings (with deviations as small as 2 Å for the mid-*Z* range) was that by Kato *et al.* [8,9], which has meanwhile been updated [10]. A wide-range HFR calculation by Biémont *et al.* [13] incorporated a fit of atomic structure parameters to the experimental data. This, in a way, supersedes the interpolation provided by Porto *et al.* [12]. The latest published calculation, by Froese Fischer and Fritzsche [18], provides calculational results only for those ions that have been studied at the NIST EBIT (which is neither the majority of the available data nor a selection of the most precise). In spite of the large calculational effort, the results are not as close to experiment as those obtained by Kato *et al.*, though clearly better than those presented by Beck.

A common problem to all these calculations is the high-*Z* range with too few experimental results to compare with. While MCDF calculations (like those done by Kato *et al.*) are expected to do best at high *Z*, the mismatch of their results with the experimental wavelengths increases above $Z=74$. Even worse is the mismatch of the HFR calculations at the highest-*Z* values covered, probably because the relativistic contributions are no longer a correction, but dominant. In this situation, precise experimental data are of utmost importance to challenge theory. Our wavelength numbers (Table I, Fig. 3) are about four to five times more precise than any of the others in the high-*Z* range. Our earlier result for Au [3] is improved upon by a factor of 20. Our previously presented result for W is more precise than the data from the NIST EBIT by a factor of about 20 [12], and better by a factor of 5 than the data obtained at the Tokyo EBIT [10], all three results being published within a year of each other. Only because of the high precision of our data for W, Pt, and Au is it possible to make at least an educated guess about which of the two lines observed in Tl is the likely better candidate. If confirmed, this identification would imply a clear guideline for future improvements of the presently best calculations in this high-*Z* range.

It would be interesting to continue such measurements in the region of even higher *Z*. Unfortunately, the transition of interest should be rather weak in that range, due to the increasing competition by another decay branch, the $J=4$-3 transition. Consequently, the success of such measurements will depend even more on the use of high-efficiency optics. The present measurement shows that this should be possible even if the emitted intensity decreases by an order of magnitude.

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