

Compilation of Wavelengths and Energy Levels of Tungsten, W III through W LXXIV

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Abstract

The methods used to critically evaluate and compile the data on energy levels, wavelengths, and ionization potentials of multiply ionized tungsten and other ions and atoms are described. Some examples of the problems occurring in the process of data evaluation are given.

Keywords:

wavelength, energy level, ionization potential, highly charged ion, level optimization, parametric calculation

1. Introduction

Tungsten is important for controlled fusion research as a prospective construction material for tokamaks. Diagnosing its ions in the tokamak plasma requires detailed knowledge of their spectra. The spectra W I through W VII were studied the most thoroughly. The recently completed compilation of energy levels, wavelengths, and transition probabilities of W I and W II [1] contains 771 energy levels and 9887 lines. Critical compilation of spectral data for higher ionization stages of tungsten is currently underway at the National Institute of Standards and Technology (NIST). For the spectra W III through W VII, studied using a sliding-spark light source, there are now several hundreds of known lines. Other light sources such as laser-produced plasmas, exploding wires, tokamaks, and electron-beam ion traps (EBITs) produce higher ionization stages. Some experimental data exist now for W¹³⁺, W²⁷⁺ through W⁴⁸⁺, and W⁵²⁺. Some of the highly ionized species of tungsten were extensively studied by several teams. However, in many cases the information for the energy levels involved in the observed transitions is absent, fragmentary, or ambiguous.

The available ionization potentials (IPs) for most species of tungsten were calculated with uncertainties of about 5%. This is insufficient for plasma-diagnostic applications. A semi-empirical method developed at NIST allowed us to obtain the IPs with uncertainties as small as 0.01%.

The methods that we use to critically evaluate and

compile the data for tungsten are similar to those used for other elements. We select the most accurately measured wavelengths and derive the energy levels that are consistent with them. For complex spectra, the level optimization problem requires a special treatment. A computer code LOPT [2] that implements the least-squares method to find the optimal energy levels was developed at NIST for this purpose. To resolve line-assignment ambiguities, we make *ab initio* and semi-empirical calculations of atomic structure and transition rates. For the Na-, Ne-, He-, and H-like ions, where there are no measurements, we include the published results of accurate calculations, as these spectra are important for plasma diagnostics and benchmark theory-testing experiments.

2. Semi-empirical calculation of IPs

For multiply ionized tungsten, the only available experimental IP values exist for W⁴⁺ [3], W⁵⁺ [4], W⁶⁺ [5], and W⁴⁵⁺ [6-8]. Accurate values of the IP were obtained for Ni-like W⁴⁶⁺ [7] by means of an isoelectronic interpolation and for He-like W⁷²⁺ [9] and H-like W⁷³⁺ [10] by means of precise *ab initio* calculations. For the rest of the tungsten spectra, the best available values of the IP were calculated by Carlson *et al.* [11] in a simple approximation. Their uncertainty is 5%.

An accurate semi-empirical method of calculating the IPs [12] was developed at NIST. It is based on the suite of codes of R. Cowan [13]. These codes are widely

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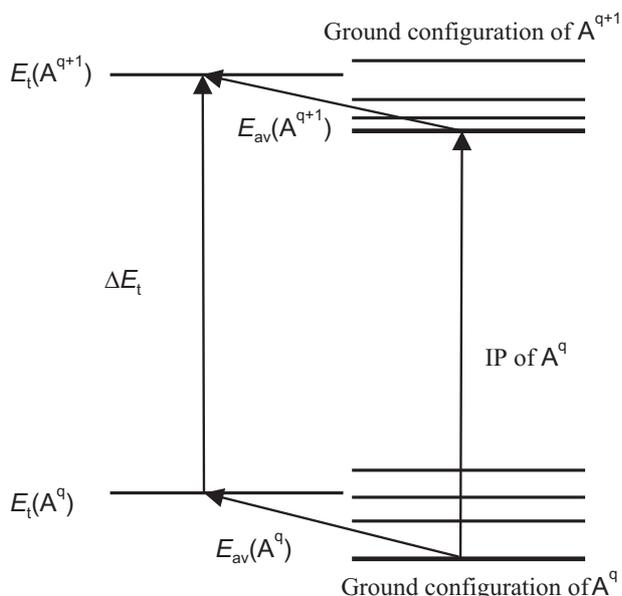


Fig. 1 Calculation of IP of an ion A^q . E_t are the total energies of the ground configurations of the successive ions A^q and A^{q+1} , E_{av} are the average energies of the ground configurations.

used to calculate the energy levels and transition rates of atoms and ions. It is well known that the accuracy of *ab initio* calculations done with these codes is not very high (for energy levels and IPs, it is usually a few percent). However, these codes proved to be extremely successful in analyses of complex spectra because of their capability to use empirically adjusted parameters (the Slater integrals). With empirically adjusted parameters, Cowan's codes can reproduce the experimentally determined energy levels with uncertainties of a few hundredths of a percent, which is often impossible to achieve with any existing *ab initio* code. Calculation of the IP of an arbitrary ion A^q by means of Cowan's codes is illustrated in Fig. 1. The quantity ΔE_t , called the *binding energy* of the ground configuration of A^q , is the difference of the total energies of the ground configurations of the two successive ions A^q and A^{q+1} . Cowan's code RCN calculates the total energies in the single-configuration Hartree-Fock approximation with approximate relativistic corrections. The fine-structure splitting of the ground configurations is calculated by Cowan's code RCG. The shift of the energy of the ground state relative to the center of gravity of the ground configuration is called the *average energy* of the ground configuration. Then the IP is calculated as $IP(A^q) = \Delta E_t + E_{av}(A^q) - E_{av}(A^{q+1})$. The binding energy often represents the largest contribution to the IP. The uncertainty of its calculation with the RCN code is usually between 1% and 5%. To reduce these uncertainties, we use semi-empirical scaling of the bind-

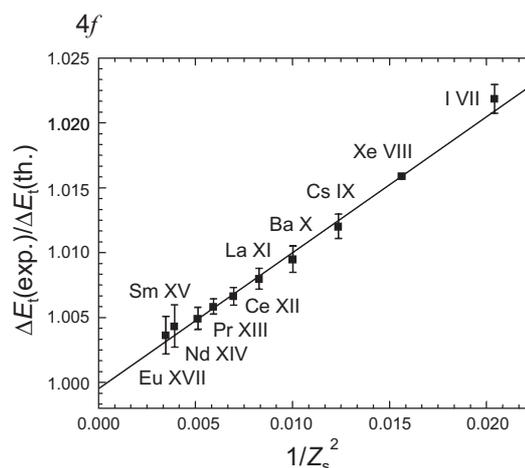


Fig. 2 Isoelectronic comparison of empirical scaling factors for the 4f binding energies in Ag-like ions. Z_s is the number of the spectrum. The error bars represent the experimental uncertainties of the IPs. The solid line is a linear fit.

ing energies. The scaling coefficients are determined from other spectra where the IPs are known experimentally. An example of such determination is presented in Fig. 2. For the Ag I sequence, the isoelectronic behavior of the scaling coefficients is very smooth and proportional to $1/Z_s^2$, where Z_s is the spectroscopic charge of the ion (for Ag-like W XXVIII, $Z_s = 28$). From this dependence, the binding energy of the 4f electron can be determined with relatively small uncertainty for any member of the sequence. The IP of W^{27+} determined from the scaled 4f, 4d, and 5s binding energies is $(7110 \pm 13) \cdot 10^3 \text{ cm}^{-1}$. Using similar methods of scaling the binding energies, the IPs of all stages of ionization of tungsten were calculated with greatly improved accuracy.

3. Classification of lines

Many of the highly-ionized species of tungsten were experimentally studied in recent years. Consequently, there are many unique observations that were not repeated and verified by other teams. In such cases we verify the line identifications by calculating the energy levels, transition wavelengths, and radiative rates for the studied spectrum.

An example of this situation is the Pm-like spectrum W XIV. Hutton *et al.* [14] recently reported an observation and identification of the $4f^{14}5s^2S - 4f^{14}5p^2P_{3/2, 1/2}^o$ doublet at $365.3 \pm 0.2 \text{ \AA}$ and $258.2 \pm 0.2 \text{ \AA}$ in an EBIT. Their identification was based on the prediction of the collapse of the 4f shell along the Pm I isoelectronic sequence made by Curtis and Ellis [15] and on Dirac-Fock calculations by Theodosiou and Raftopou-

Table 1 Energy levels of the $4s^2 4p^3$ configuration of W XLII

Level (10^3 cm^{-1})	J	Percentage composition.	New label
0.0	3/2	47 % $^2P^o + 27 \%$ $^2D^o + 26 \%$ $^4S^o$	$^2D^o$
719.6	3/2	55 % $^4S^o + 45 \%$ $^2D^o$	$^4S^o$
762.1	5/2	100 % $^2D^o$	$^2D^o$
[808]	1/2	100 % $^2P^o$	$^2P^o$
[1537]	3/2	52 % $^2P^o + 28 \%$ $^2D^o$	$^2P^o$

los [16]. Curtis and Ellis [15] stated that the ground state of Pm-like ions, starting with W^{13+} , is $4f^{14}5s^2 S_{1/2}$. This would make the spectrum very simple and similar to other single-electron spectra. However, Theodosiou and Raftopoulos [16] predicted that the ground state of W^{13+} and Ir^{14+} would be the odd-parity $4f^{13}5s^2 \ ^2F_{5/2}^o$. We calculated the W^{13+} spectrum by means of Cowan's codes [13], and the results were in perfect agreement with those of [16]. Hence, this spectrum should be much more complex, with the $4f^{14}5s^2 S - 4f^{14}5p \ ^2P_{3/2,1/2}^o$ lines being weaker than the numerous lines of the $4f^{13}5s^2 - 4f^{13}5s5p$ and $4f^{12}5s^2 5p - 4f^{12}5s5p^2$ transitions dominating the spectrum in this region. Therefore, the identifications of Hutton *et al.* [14] need confirmation, and we do not include them in our tables.

The situation with the As-like spectrum W XLII illustrates cases where it is necessary to carefully consider how the levels are to be designated. Asmussen *et al.* [17] observed the lines at 46.9 Å, 60.6 Å, 64.9 Å, and 131.8 Å in a tokamak. They identified the first two lines as blends of W^{41+} and other stages of ionization. The line at 64.9 Å was classified as the $4s^2 4p^3 \ ^4S_{3/2}^o - 4s4p^4 \ ^4P_{5/2}$ transition, the lower level being the ground state. The line at 131.8 Å was classified as the magnetic-dipole (M1) transition $4s^2 4p^3 \ ^4S_{3/2}^o - 4s^2 4p^3 \ ^2D_{5/2}^o$. Table 1 shows the level composition of the $4s^2 4p^3$ configuration resulting from our parametric fitting. It is difficult to assign distinct names to the $J = 3/2$ levels. In this case we have chosen to assign the names given in the last column of Table 1. Although not perfect, this seems to be the most reasonable way of designating these levels. Nevertheless, it is important for users to be aware of these problems and to consult the percentage composition of the levels.

In addition to the level-naming problem, the $J = 5/2$ assignment of the upper level of the M1 line at 131.8 Å does not agree with our calculations of the transition rates. Our calculations indicate that the $4s^2 4p^3 \ ^2D_{3/2}^o - 4s^2 4p^3 \ ^4S_{3/2}^o$ transition (i.e., between the ground state and the first excited level) has a much greater radiative rate. The identifications of the allowed transitions

were confirmed by Radtke *et al.* [18] except for the level designations. Using an EBIT, they re-measured the wavelengths with lower uncertainties and succeeded to distinguish the emission of W^{41+} from the neighboring stages of ionization that were blending the lines observed in [17]. Radtke *et al.* used *jj*-coupling notation for all levels. Their designations, although unambiguous, are not easy to identify with those of [17].

Utter *et al.* [19] re-measured the W^{41+} lines observed by Radtke *et al.* with much lower uncertainties using an EBIT. They observed three more lines that they associated with the $4s^2 4p^3 - 4s^2 4p^2 4d$ array. However, their designation of the levels is ambiguous. For example, the upper level of the line at 51.091 Å was denoted as $4p_{1/2} 4p_{3/2} 4d_{3/2} (J = 3/2)$. The two p electrons can combine differently, so their aggregate angular momentum can be either 1 or 2. As this intermediate state is not specified, the reported designation is incomplete. In order to determine what level is actually associated with this and other transitions, we calculated the W^{41+} spectrum with Cowan's codes [13] and found a very good agreement of predicted and observed wavelengths and relative intensities of the lines. The upper level of the above-mentioned transition turned out to be $4s^2 4p^2 ({}^3P_1) 4d(1, 3/2)_{3/2}$.

Similar problems are encountered in Br-, Kr-, Rb-, Se-, Ge-, and Ga-like spectra. In all cases, Cowan's codes proved to be a very powerful tool in the data evaluation.

4. Level optimization

Complex spectra often have a large number of lines connecting a much lower number of energy levels with each other. In such cases, deriving the energy levels from the wave numbers of the observed transitions is a non-trivial task. Even when the energy levels were already determined by the authors who made the spectrum analysis, we often proceed to re-determine the levels in order to verify the energy values and to detect possible misidentifications. For this purpose, there are two different least-squares fitting codes, ELCALC [20] and LOPT [2]. The well-known and widely used EL-

CALC code makes iterations, on each cycle adjusting the energy levels so as to minimize the sum of squares of weighted deviations of Ritz wave numbers from the observed ones. The LOPT code solves the least-squares problem by another method. The problem is represented by a system of linear differential equations expressed in the form of a matrix equation. This equation is solved by inverting the matrix. The advantage of this method is that, simultaneously with the level optimization, it calculates the uncertainties of the Ritz wave numbers. Thus, in a single run of the code, not only the energy levels are obtained, but also the uncertainties of the predicted wavelengths of all observed lines. If the newly optimized energy levels reasonably agree with the original values determined by the authors of the analyses, we accept the original energy levels. Otherwise, we revise the levels and use our optimized energies and Ritz wave numbers.

5. Conclusion

By using the set of powerful analytical and data-processing tools available at NIST, we critically evaluated and compiled an extensive set of energy levels, wavelengths, and IPs of all stages of ionization of tungsten. The data tables, details of the analysis, and bibliography on these spectra will be published elsewhere in full reports and given in the NIST Atomic Spectra Database (<http://physics.nist.gov/PhysRefData/ASD>).

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References

- [1] A.E. Kramida and T. Shirai, *Submitted to J. Phys. Chem. Ref. Data* (2004).

- [2] A.E. Kramida and G. Nave, *Eur. Phys. J. D* **37**, 1 (2005).
- [3] S.S. Churilov, R.R. Kildiyarova and Y.N. Joshi, *Can. J. Phys.* **74**, 145 (1996).
- [4] J. Sugar and V. Kaufman, *J. Opt. Soc. Am.* **69**, 141 (1979).
- [5] J. Sugar and V. Kaufman, *Phys. Rev. A* **12**, 994 (1975).
- [6] J. Reader and G. Luther, *Phys. Scr.* **24**, 732 (1981).
- [7] N. Tragin *et al.*, *Phys. Rev. A* **39**, 2085 (1989).
- [8] J.F. Seely, C.M. Brown and W.E. Behring, *J. Opt. Soc. Am. B* **6**, 3 (1989).
- [9] D.R. Plante, W.R. Johnson and J. Sapirstein, *Phys. Rev. A* **49**, 3519 (1994).
- [10] W.R. Johnson and G. Soff, *At. Data Nucl. Data Tables* **33**, 405 (1985).
- [11] T.A. Carlson, C.W. Nestor Jr., N. Wasserman and J.D. McDowell, *At. Data. Nucl. Data Tables* **2**, 63 (1970).
- [12] S.S. Churilov, Y.N. Joshi, J. Reader and R.R. Kildiyarova, *Phys. Scr.* **70**, 126 (2004).
- [13] R.D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley - Los Angeles - London, 1981).
- [14] R. Hutton *et al.*, *Nucl. Inst. Methods Phys. Res. B* **205**, 114 (2003).
- [15] L.J. Curtis and D.G. Ellis, *Phys. Rev. Lett.* **45**, 2099 (1980).
- [16] C.E. Theodosiou and V. Raftopoulos, *Phys. Rev. A* **28**, 1186 (1982).
- [17] K. Asmussen *et al.*, *Nucl. Fusion* **38**, 967 (1998).
- [18] R. Radtke *et al.*, *Phys. Rev. A* **64**, 2720 (2001).
- [19] S.B. Utter, P. Beiersdorfer and E. Träbert, *Can. J. Phys.* **80**, 1503 (2002).
- [20] L.J. Radziemski, Jr. and V. Kaufman, *J. Opt. Soc. Am.* **59**, 424 (1969).