Energy Levels of Singly Ionized and Neutral Zirconium

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Abstract

Improved energy levels for singly ionized and neutral zirconium of both even and odd parity are determined from Fourier Transform Spectrometer data using a least-squares optimization procedure. Data from interferometric spectrometers provides much tighter control of systematic uncertainties in line position measurements than was achieved using older (e.g. Rowland Circle) dispersive spectrometers.

1. Introduction

Energy levels for neutral and ionized atoms are available in the National Institute of Standards and Technology (NIST) Atomic Spectra Database (ASD). Energy levels for singly ionized and neutral atoms are more complete than levels for more highly ionized species because both singly ionized and neutral species are found in Hollow Cathode Discharges (HCDs) which are convenient spectroscopic sources for laboratory studies. The singly ionized and neutral Zirconium (Zr) energy level precision is **0.01 cm^{-1}** in the ASD by Kramida et al. (2021) **[1]. The NIST ASD energy levels for neutral Zr are originally from Kiess & Kiess (1931) [2] and Meggers & Keiss (1932) [3] via Moore (1952) [4] and similarly for singly ionized Zr from Kiess & Kiess (1930) [5] via Moore (1952) [4]. The 0.01 cm^{-1} precision** is satisfactory for efficiently finding Zr II and Zr I lines. **Wavelengths in the original 1930-1932 papers are reported to 0.001 nm. Using this as an uncertainty and a wavelength of 500 nm corresponds to ~0.04 cm^{-1} wavenumber uncertainty for strong lines of singly ionized Zr. Neutral Zr has its strong lines somewhat more to the red and thus could have a smaller uncertainty of ~0.03 cm^{-1}. Energy level uncertainties are expected to be of similar or smaller size as the spectral line uncertainties. Although these seem like reasonable uncertainties, a comparison of older dispersive measurements with more modern interferometric measurements is still desirable. The NIST Help Pages state: "***If no energy level uncertainty is available in the ASD, it is usually safe to assume that the probable error is between 2.5 and ~25 units in the least significant digit. About 90% of energy levels in ASD satisfy this assumption.*"[2]

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[2] NIST ASD Help Pages at https://physics.nist.gov/PhysRefData/ASD/Html/levelshelp.html

The element Zr is not unique among heavier elements. In many cases older, dispersive or grating spectrometer (e.g. Rowland Circle), data is used to determine energy levels in the ASD. The widespread availability of data from interferometric Fourier Transform Spectrometers (FTSs) creates an opportunity to improve energy levels to **0.001 cm^{-1}** or perhaps a bit better (Learner & Thorne (1988) [**6**].) In this study, measured line Center of Gravity (COG) values for Zr II (the second spectrum or singly ionized Zr) and for Zr I (the first spectrum or neutral Zr) from publically available FTS data are used to improve the energy levels to ~**0.001 cm^{-1}.**

Several research areas benefit from improved energy levels. In laboratory spectroscopy there is a need for accurate Ritz (energy level difference) line positions to resolve line blends. An example can be found in the analysis of lab spectra to determine accurate atomic transition probabilities. Line blends must be resolved in some fashion to use the radiative lifetime + branching fraction (BF) method e.g., [**7**]. The Wisconsin Atomic Transition Probability (WATP) program used this method extensively. Branching ratios (BRs) for lines from a single upper level, which sum to unity, are called BFs. BFs divided by radiative lifetimes from laser induced fluorescence measurements provide reliable atomic transition probabilities. One of the simplest and most efficient methods for blend separation is sometimes called the COG method. In this method the COG of the blended feature is compared to Ritz values for the wavenumbers of the transitions. Accurate Ritz wavenumbers for the desired spectral line and for the blending spectral line are necessary along with a high resolution and high signal to noise ratio (SNR) lab spectrum from a FTS or a similar spectrometer. A single equation with a single unknown is used to determine the absolute fraction of the blended feature from the line of interest.

The WATP program has used the COG method to separate blends in two recent transition probability studies in Fe II [**8**] and in Hf II [**9**].

Our interferometric COG measurements on hafnium were shared with the NIST ASD prior to publication [10] and were useful in improving the more comprehensive NIST ASD energy levels for neutral hafnium now available. **Our primary goal is to help astronomers when trying to resolve blends or to extract an isotopic abundance pattern from a spectrum of a distant star recorded with the next generation of extremely large, 30 to 50 m diameter, telescopes. Extremely large telescopes, even ground based, will provide better spectroscopic data on distant stars.**

2. Spectra and Calibration

One of the important features of FTS data is the exceptionally linear wavenumber scale. With a proper compensator (to cancel the dispersion of a thick beam splitter) and a good phase correction, only a “rubber ruler” or multiplicative correction near unity is needed for an accurate wavenumber scale. **It is now standard to base** this multiplicative correction on selected Ar II lines **identified** by Learner & Thorne (1988) [**6**]. The correction removes the effect of slight misalignment (on the order of 10^{-3} to 10^{-4} radians) between the lamp beam and calibration laser beam and removes the effect of the FTS aperture. The linearity of interferometric or FTS data is important to the control of systematic uncertainties in COG transition wavenumbers. **This is summarized in the first equation** of Aldenius (2009) [11] $\boldsymbol{\sigma}_{corr} = (1 + k_{eff})\, \boldsymbol{\sigma}_{\mathbf{obs}}$ **where σ is a wavenumber and k_{eff} is the “rubber ruler” correction.**

One of the early optical-UV FTSs was the 1m instrument built and used at Kitt Peak on the McMath Solar Telescope of the National Solar Observatory (NSO) [**12**]. This FTS was used to record many Solar **spectra** as well as 1000s of laboratory **spectra**. Although this instrument has been de-commissioned, the FTS **spectra** have all been archived and are now publically available.[3] Such **spectra** have been used to determine BFs for several decades by the WATP program, but can also be used to refine energy levels.

The WATP program did not work on Zr, but benefits from substantial experience with FTS data. A quick survey of the archived laboratory data yielded **a total of** ten **spectra** listed in Table 1. **The carriage travel value in the headers indicate that all five of the spectra recorded during 1991 are based on asymmetric interferograms. The asymmetric interferograms can result in a poor phase correction [13]. Dropping all five of the 1991 data results in too small of a set of spectra for our study. A helpful referee identified the poor phase correction in spectra 6 & 7. These two spectra were dropped in our analysis. The phase correction on spectra 8, 9 , & 10 is satisfactory.** These FTS data were all recorded on HCD lamps at low. 1.0 or 2.0 Torr, pressure. These spectra have many strong lines of Zr I and Zr II from sputtering. The **spectra** also include the strong lines of Ar I and Ar II needed for calibration. **Our primary calibration uses the now standard Ar II lines. Table 2a reports the "rubber ruler" corrections and uncertainties used spectra 1, 2, &5 which has strong Zr II lines.**

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[3] http://diglib.nso.edu/

These 28 Ar II lines are strong in HCD spectra, and are relatively insensitive to pressure shifts because the lines connect lower configurations. They were first identified by Learner & Thorne (1988) [6] as good candidates for calibration standards. They had earlier wavenumber measurements by Norlén (1973) [14], which are now superceded by measurements from Whaling et al. (1995) [15]. These 28 Ar II lines, as remeasured by Whaling et al. (1995) [15], are the primary standards used in this work. Sansonetti (2007) [**16**] checked and confirmed the Ar II standard lines as **re**measured by Whaling et al. (1995) [**15**], but disputed Ar I line wavenumbers measured by Whaling et al. (2002) [**17**]. Sansonetti's revision of the Ar I line wavenumbers was less than **0.001 cm^{-1}** in **the IR below 10,000 cm^{-1}**. **Nave & Sansonetti (2011) [18] more recently checked and confirmed the Ar II standard lines as remeasured by Whaling et al. (1995) [15]. Liggins et al. (2021) [19] have a discussion of wavenumber measurement uncertainties.**

Another source of systematic uncertainty, due to illumination shifts, was discussed, studied, and modeled by Learner & Thorne [**6**]. A different illumination of the entrance aperture of the FTS collimator by lines of Ar II and Zr could also affect Zr wavenumber accuracy by changing the path difference through the FTS. Learner & Thorne [**6**] found that emission intensities, I, of the sputtered metal and the Ar II are spatially similar, and well described by a parabolic model, $I = I_o[1 + \beta(r/r_o)^2]$ where r is the radius inside the HCD and r_o is the radius of the cathode surface. They suggest that illumination shifts should be less than 0.001 cm^{-1}. Using their model, and $\beta=0.5$ with opposite sign to describe the spatial variations of the Ar II reference lines and the Zr lines, it is possible to generate systematic uncertainties of a 0.001 cm^{-1} or slightly more.

However such large illumination shifts are perhaps not likely. Salit et al. (2004) [**20**] describe a clever experiment using an integrating sphere to avoid any illumination shift with a frequency-doubled single frequency laser. **The fundamental and** second harmonic are separated by exactly a factor of 2 **in frequency**. The wavenumber scale of an FTS is quite linear to better than **0.001 cm^{-1}** in the optical or the six ppb as reported by Salit et al. [**20**]. COG wavenumber measurements to better than **0.001 cm^{-1}** are possible, but great care is required to avoid pressure shifts, illumination shifts, and **alignment shifts**. The use of an integrating sphere could avoid any illumination shift, but HCDs are generally not sufficiently bright to overcome the signal loss of a sphere, especially in the UV. A simple current increase does increase the brightness of a HCD, but also it increases the number of self-reversed lines.

The **0.001 cm^{-1}** agreement of our Hf COG measurements from the University of Wisconsin (UW) by Lawler et al. (2022) [**10**] with independent COG measurements from Lund University by Lundqvist et al. (2006) [**21**] is reassuring. COG wavenumber measurements on lines from FTS data with a high SNR can have extremely small statistical uncertainty. Although Learner & Thorne (1988) [**6**] did a thorough study of possible systematic errors in FTS measurements of COG wavenumbers, it is necessary to consider the possibility that there is a synergistic effect between alignment and illuminations and/or pressure shifts **especially if the alignment shift is large**. This needs to be considered when FTS data is used to determine energy levels e.g. neutral Molybdenum. Although archived FTS data is significantly better than the ~90 year old data from dispersive spectrometers, it has some disadvantages **as illustrated by the poor phase correction of the two Zr/Ar spectra which were discarded.**

Wavenumber measurements are effectually wavelength or length measurements and have more sources of systematic error than time measurements. Eventually, optical frequency combs may be used to measure energy levels to much greater accuracy and precision, but it will be necessary to devise a parallel experiment and not the one line at time method in use now. Modern atomic clocks based on optical frequency combs are producing uncertainties as small as 1 part in 10^{18} or 1 sec in the age of the Universe. There is no doubt that frequency measurements could be as accurate as some small fraction of the natural line width from radiation broadening, however measurements using optical frequency combs are not massively parallel and thus are expensive. **We note that some frequency measurements using trapped ions and atomic beams are compared to FTS data in Nave & Sansonetti (2011) [18]. Such measurements are important to test standards but are not massively parallel over a wide wavelength range.** FTS instruments are now massively parallel **over a wide wavelength range.**

3. Analysis of FTS Data on Zr II

Spectra indexed (in this project) 1, 2, and 5 have both the strong Ar II lines, including most of the 28 Ar II calibration lines, and strong Zr II lines. Strong in this context means that estimated SNRs are 50 or more. The same software was used to integrate the Zr II and Ar II lines and evaluate line COGs. It is important to consider possible hyperfine structure (HFS) and isotope shifts (ISs), none of which are resolved in this study. There are five isotopes of Zr in Solar System material: ^{90}Zr (0.5145 ± 0.0004, I = 0), ^{91}Zr (0.1122 ± 0.0005, I = 5/2), ^{92}Zr (0.1715 ± 0.0003, I = 0), ^{94}Zr (0.1738 ± 0.0004, I = 0), and ^{96}Zr (0.0280 ± 0.0002, I = 0) [**22**]. Four digit fractional abundances and nuclear spins I are indicated. Only one of these isotopes, ^{91}Zr, has HFS, and ISs are typically small near the middle of the periodic table. The fact that the Zr II and Zr I lines appear sharp at the resolving power of the FTS data in Table 1 is not surprising. The isotopic makeup of Zr is presented above to remind our readers that all of our FTS results are from samples with a Solar System isotopic abundance.

A few of the strongest Zr II lines are self-reversed in some of the **spectra** of Table 1. The wavenumber COGs of self-reversed lines are not included in our analysis. The relatively low pressure, ~ 1 Torr, likely enhanced the Zr ion emission from some our **spectra**. Table 3 is our complete line list for Zr II. Table 3, included in full as Supplementary material, lists the COG wavenumbers of the 89 lines of Zr II used in our work as well as Ritz wavenumbers and wavelengths from our optimized levels. A stub table is included in our paper to provide guidance on the form and content of the asc ii table available in the Supplementary material. The asc ii machine readable format with metadata header is the format we have used for decades to make our laboratory data easily accessible. The primary advantage of asc ii over other formats is that it is low-level and will have longest lifetime and is now useable by any software.

The method we used for generating a least-squares optimized set of energy levels for singly ionized Zr is similar to that described by Kramida (2011) [**23**]. A weighted matrix is generated from the measured COG wavenumbers. The weight factors are the square of the inverse of the uncertainty of the **weighted** average COG wavenumber. The same method is used here **for both Zr II and Zr I.** The small number of **spectra** contributing to the average COG results in **an unreliable uncertainty from a standard deviation as discussed by Liggins et al. (2021) [19]. Our uncertainties are based on the SNRs of COG measurements and the uncertainty of the "rubber ruler"**

correction in Table 2. This approach is similar to that described by Liggins et al. (2021) [19] who states: "*A minimum value of 1 /* $\sqrt{\sum_i \delta_i^{-2}}$ [, where δ_i is the total uncertainty of a COG measurement in a single spectrum given by the sum of the statistical and calibration uncertainties,] *was placed on the uncertainty in the weighted averaged wavenumber so that, should a small number of measurements happen to very closely coincide, the resulting uncertainty would not be unreasonably low.*"

Th**e** matrix is nearly 100x100 in our Zr I work described below, and could be larger. To accurately invert the matrix, it must be well conditioned. Our system of conditioning the matrix follows Graybill (1961) [**24**] and results in a Cholesky decomposition method similar to, but more robust than, that described by Kramida [**23**]. Some simple matrix inversion techniques that are used with small matrices do not produce accurate results for large matrices. After operation of the inverted matrix on a vector constructed from measured COG wavenumbers, energy levels from the COG measurements are determined. The reader may find the description in Lawler et al. [**10**] more useful for details. Finally, Uncertainties D1 and D2 are determined. The uncertainty D1 is typically smaller than D2. Kramida [**23**] described the evaluation of D1 which is typically a minimum uncertainty of a level with respect to nearby levels connected by strong dipole allowed transitions, whereas D2 is an uncertainty of the level with respect to the ground level.

A final uncertainty can be included which may be systematic. The Ar II calibration lines from Whaling et al. (1995) [15] all have an uncertainty of 0.0002

cm^{-1} and wavenumbers of ~20000 cm^{-1}. If the 0.0002 cm^{-1} is a random uncertainty then it can be combined with other uncertainties on our energy levels using quadrature. If the 0.0002 cm^{-1} is a systematic uncertainty, e.g. from FTS alignment used by Whaling et al., affecting all of our COG measurements in a similar fashion, then it should be combined with other uncertainties using simple addition. Table 4, Table 5, and subsequent energy level Tables have D2 uncertainties including the more conservative simple addition of a calibration slope uncertainty of 1xE-8 multiplied by the energy level. Liggins et al. (2021) [19] similarly added this possible systematic uncertainty with the statement: "Finally, an uncertainty of 1 × 10−8 times the wavenumber or wavelength was added to all the uncertainties to account for the uncertainty of the original Ar II standard lines.". This may affect D1 in proportion to the wavenumber of a connecting transition, but it is small and has not been included in D1.

Tables 4 and 5 present our refined energy levels for even and odd parity levels of singly ionized Zr, respectively. Also given are energy levels from the NIST ASD for the 36 levels in common. **The average difference was 0.026 cm^{-1} with a standard deviation of 0.093 cm^{-1}.**

Although we have based our uncertainty estimates on our observed SNR and on published uncertainties of reference Ar II reference lines, a reliable estimate of systematic uncertainty is often determined using a comparison of independent results. Independent in this context means a different instrument or FTS, different software, and different personnel. A thorough search of the NIST website revealed an unpublished set of energy level determinations from lines of Zr II from FTS data.[4] These unpublished results, from Sveneric Johansson, agree with our energy levels significantly better than they agree with the energy levels of the NIST ASD.

4. Analysis of FTS Data on Zr I

The **spectra** in Table 1 including 3, 4, 8, 9, and 10, that lacked strong Zr II lines have strong Zr I lines. Many of the strong Zr I lines are in the near IR. Unfortunately, the near IR spectra do not include the preferred Ar II lines for calibration. Our initial calibration was based on lines of Ar I measured by Whaling et al. (2002) [**17**]. Approximately 70 lines of Ar I with wavenumber uncertainties of **0.0007 cm^{-1}** or less and a log(SNR) of 5 or more were used. This initially seemed reasonable because the **lines at 10,000 cm^{-1} and below** were measured to better than **0.001 cm^{-1}**, even with a small correction from Sansonetti (2005) [**16**]. However, many of the IR calibration lines connect to relatively high (Rydberg like) configurations of neutral Ar. This suggests that we need to be concerned about pressure induced line shifts. A careful search did not reveal any reliable measurements or calculations on the pressure induced shifts of IR Ar I lines from Ar collisions.

The obvious need to test our calibration led to a new calibration. We picked a bootstrap calibration which is based on the Ar II calibration of **spectra** 1, and 2 combined with strong lines in common with **spectra** 3, and 4. Strong Ar I lines on spectra 3, 9, and 10 were used to transfer the calibration to **spectra** 9, and 10. It is expected that the strong lines of Zr II and Zr I connected to low configurations are less shifted by Ar collisions

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[4] https://physics.nist.gov/PhysRefData/Handbook/Tables/zirconiumtable6.htm

than the Ar I lines connected to higher (Rydberg like) configurations. **Although Zr lines connecting lower configurations should have lower pressure shifts, the strength and distribution of Zr lines were not as favorable as Ar I lines for transferring the calibration.** A total of 39 lines were used that are common to **spectra** 3 and to **spectra** 9, and 10. Table 2b includes the "rubber ruler" or wavenumber scale multiplicative calibration factor for **spectra** 3, 4, 8, 9 and 10 from our initial Ar I calibration and our bootstrapped Ar II calibration which we used. **These calibrations factors are very similar, but not identical due to pressure shifts of the Ar I lines. Pressure induced line shifts of Ar I lines are included in the calibration in Table 2c for the 2 Torr spectra 8, 9, & 10.** A careful inspection of Table 2 shows that pressure shifts are likely negative and comparable in magnitude and in sign to those studied by Veza et al. (2012) [**25**]. The change in the COG wavenumbers of Zr I lines from the wavenumber scale change in Table 2 **is less than 0.0026 cm^{-1}** at 10,000 cm^{-1}.

It is tempting to claim that our calibration yields pressure shift coefficients for lines connecting the 5s, 4f, and 3d configurations to the 4p and 3d configurations. Unfortunately, the scatter in our calibration measurements means that any pressure shifts extracted would have large uncertainties.

Table 6 lists the COG wavenumbers of the 372 lines of Zr I lines used in our work as well as Ritz wavenumbers and wavelengths from our optimized levels. As with Table 3, Table 6 is included in full as Supplementary material, and is in machine readable asc ii format with metadata header. A stub table is included in our paper to provide guidance on the form and content.

The method we used for generating a least-squares optimized set of energy levels of neutral Zr is identical to that discussed earlier for Zr II. Tables 7 and 8 present our refined energy levels for even and odd parity levels, respectively, of neutral Zr. Also given are NIST ASD energy levels for the 87 levels in common.

The NIST ASD energy levels of Zr are more complete than the improved energy levels reported herein. However, blending problems and isotopic abundance studies are likely to benefit from improved energy levels of this study.

5. Conclusion

We report improved energy levels for 36 levels of singly ionized Zr and 87 levels of neutral Zr. These improved energy levels are from interferometric data recorded using a FTS. For the 36 levels of single ionized Zr, the differences between our refined energy levels and those listed in the NIST ASD range from **-0.164 cm^{-1}** to **+0.229 cm^{-1}**. The average difference is **0.026 cm^{-1}** with a standard deviation of **0.093 cm^{-1}**. For the 87 levels of neutral Zr, the differences between our refined energy levels and those listed in the NIST ASD range from **-0.116 cm^{-1}** to **+0.195 cm^{-1}**. The average difference is **0.031 cm^{-1}** with a standard deviation of **0.065 cm^{-1}**. These differences **indicate that energy level uncertainties based on wavelength uncertainties of 0.001 nm from the ~90 year old data are too optimistic. However, they** are all within the target NIST accuracy of 25 times the least significant digit in the ASD. The Zr I, II energy levels currently in the NIST ASD are sufficiently accurate to find lines, but will not be sufficiently accurate for future research. The utility of improved energy levels is to be found in both laboratory spectroscopy and in astrophysical spectroscopy. Blend separation is important, and the possibilities for more and better isotopic abundance determinations should be improved with the extremely large telescopes being designed and built today.

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Table 1. Fourier transform spectra of Zr/Ar hollow cathode discharge lamps found for this study.

Project Serial No.	Date	NSO Serial No.	Ar pressure (Torr)	Lamp Current (mA)	Wavenumber Range (cm^{-1})	Limit of Resolution (cm^{-1})	Coadds	Beam Splitter	Filter	Detector[1]
1	1988 Nov. 15	1	1	770	8433 - 39979	0.038	5	UV		S. B. Si Diode
2	1988 Nov. 15	2	0.7	151	8433 - 39979	0.038	5	UV		Midrange Si Diode
3	1988 Nov. 15	3	1	825	3593 - 12009	0.012	4	UV	GaAs	InSb
4	1988 Nov. 15	4	1.03	825	8360 - 20002	0.019	4	UV	OG515	InSb
5	1988 Nov. 15	5	1.03	825	14865 - 36081	0.036	4	UV[2]	$CuSO_4$	Midrange Si Diode[2]
6	1991 Oct. 8	1	2	500	15154 - 36081	0.044	4	UV	$CuSO_4$	S. B. Si Diode
7	1991 Oct. 8	2	2	500	15154 - 36081	0.044	4	UV	$CuSO_4$	S. B. Si Diode
8	1991 Oct. 8	3	2	525	7810 - 25033	0.031	8	UV	GG495	S. B. Si Diode
9	1991 Dec. 10	1	2	500	1824 - 9161	0.011	4	CaF_2	Si	InSb
10	1991 Dec. 10	2	2	500	1824 - 9161	0.011	4	CaF_2	Si	InSb

[1] Detectors types include the Midrange Si photodiode, Super Blue (S. B.) Si photodiode, and InSb.

[2] The header file of Project Spectrum 5 has errors. The Beam Splitter is listed as "MID-RANGE0" which likely refers to the detector. The UV Beam Splitter used during the first four spectra of that day was probably not changed. Lines appear in the visible which means that some sort of Si photodiode was used and not the InSb detector listed in the header.

Table 2a. Wavenumber scale correction factors from standard Ar II calibration lines.

spectrum	Multiplicative correction factor - 1 from standard Ar II calibration lines
1	(3.06 ± 0.14) x 10^{-7}
2	(2.84 ± 0.17) x 10^{-7}
5	(3.40 ± 0.16) x 10^{-7}

Table 2b. Wavenumber scale correction factors from Ar I lines and boot-strapped from standard Ar II calibration lines.

spectrum	Multiplicative correction factor - 1 Ar I calibration	Multiplicative correction factor - 1 Ar II boot-strap from spectrum 1&2
3	(3.38 ± 0.15) x 10^{-7}	(4.92 ± 0.39) x 10^{-7}
4	(3.9 ± 0.4) x 10^{-7}	(4.486 ± 0.22) x 10^{-7}
8	does not extrapolate to zero	(-5.1 ± 0.3) x 10^{-7}
9	(-2.53 ± 0.14) x 10^{-7}	(-9.0 ± 4.5) x 10^{-8}
10	(-2.47 ± 0.15) x 10^{-7}	(-8.2 ± 4.5) x 10^{-8}

Table 2c. Wavenumber scale correction factor from standard Ar II calibration lines with an adjustment for the pressure shift of the Ar I lines in spectrum 1 & 2.

spectrum	Multiplicative correction factor - 1 Ar II boot-strap from spectrum 1 & 2 with an adjustment for the pressure of spectrum 3 (1 Torr) vs 8,9,10 (2 Torr)
8	(-1.7 ± 0.3) x 10^{-7}
9	(2.5 ± 0.5) x 10^{-7}
10	(2.5 ± 0.5) x 10^{-7}

Table 3 Observed center-of-gravity Zr II transition wavenumbers and Ritz wavenumbers and wavelengths in air organized by increasing wavelength

NIST ASD			this study					
				Observed Center-of-Gravity Transition Wavenumbers (cm^{-1})				
Upper Level[a] (cm^{-1})	Lower Level[a] (cm^{-1})	Ritz wavenumber[a] (cm^{-1})	spectra used[b]	weighted mean[c]	unc.[d]	Ritz Wavenumber (cm^{-1})	unc. (cm^{-1})	Ritz wavelength in air[e] (Å)
32256.71	0.00	32256.71	1,2,5	32256.7458	0.0011	32256.7452	0.0006	3099.2273
31981.25	0.00	31981.25	1,2,5	31981.3206	0.0011	31981.3214	0.0008	3125.9190
32256.71	314.67	31942.04	1,2,5	31942.0725	0.0011	31942.0717	0.0006	3129.7602
31866.49	763.44	31103.05	1,2,5	31103.0685	0.0010	31103.0668	0.0007	3214.1886
31249.28	314.67	30934.61	1,2,5	30934.6173	0.0012	30934.6172	0.0007	3231.6916
31160.04	314.67	30845.37	1,2,5	30845.3556	0.0011	30845.3545	0.0005	3241.0440
30551.48	0.00	30551.48	1,2,5	30551.4707	0.0010	30551.4717	0.0006	3272.2216
31866.49	1322.91	30543.58	2	30543.7657	0.0011	30543.7669	0.0007	3273.0471

Notes

[a] Upper and lower level energies and Ritz wavenumber used to identify transitions are taken from NIST ASD (Kramida et al. 2021)

[b] Numbered as in Table 1

[c] SNR used as weighting factor for calculation of the mean

[d] Uncertainty estimated from transition SNR and wavenumber calibration uncertainty of spectra contributing to mean

[e] Wavelength in air is calculated from the Ritz wavenumber and the standard index of air from equation 3 of Peck & Reeder (1972)

(This table is available in its entirety in machine readable form in the Supplementary material)

Table 4.

Improved even parity energy levels of singly-ionized zirconium.

Configuration	Term	J	NIST Level (cm^{-1})	Levels from UW COGs (cm^{-1})	D1 Uncertainty of Levels[a] from UW COGs (cm^{-1})	D2 Uncertainty of Levels[a] from UW COGs (cm^{-1})	Number of lines connected to level
4d^2(^{3}F)5s	a ^{4}F	$^3/_2$	0.00	0.000	defined	Not applicable	7
		$^5/_2$	314.67	314.6735	0.0004	0.0007	10
		$^7/_2$	763.44	763.4278	0.0007	0.0009	6
		$^9/_2$	1322.91	1322.7277	0.0007	0.0011	5
4d^3	b ^{4}F	$^3/_2$	2572.21	2572.3743	0.0007	0.0008	6
		$^5/_2$	2895.05	2895.0979	0.0005	0.0008	7
		$^7/_2$	3299.64	3299.7316	0.0005	0.0009	6
		$^9/_2$	3757.66	3757.7294	0.0006	0.0012	4
4d^2(^{1}D)5s	a ^{2}D	$^3/_2$	4248.30	4248.1658	0.0006	0.0009	4
		$^5/_2$	4505.50	4505.4991	0.0007	0.0010	4
4d^2(^{3}P)5s	a ^{2}P	$^1/_2$	5724.38	5724.1506	0.0009	0.0011	3
		$^3/_2$	6111.70	6111.5316	0.0014	0.0011	3
4d^2(^{3}F)5s	a ^{2}F	$^5/_2$	5752.92	5752.8712	0.0005	0.0008	6

		$^{7}/_{2}$	6467.61	6467.5115	0.0006	0.0009	6
$4d^{2}(^{3}\mathrm{P})5s$	a ^{4}P	$^{1}/_{2}$	7512.67	7512.729	0.003	0.003	1
		$^{3}/_{2}$	7736.02	7736.106	0.003	0.003	1
		$^{5}/_{2}$	8058.16	8058.2281	0.0019	0.0022	1
$4d^{3}$	a ^{2}G	$^{7}/_{2}$	7837.74	7837.5506	0.0017	0.0014	3
		$^{9}/_{2}$	8152.80	8152.6419	0.0009	0.0013	1
$4d^{3}$	b ^{4}P	$^{1}/_{2}$	9553.10	9553.076	0.002	0.002	1
		$^{3}/_{2}$	9742.80	9742.8409	0.0009	0.0012	2
		$^{5}/_{2}$	9968.65	9968.662	0.002	0.002	1
$4d^{3}$	a ^{2}H	$^{11}/_{2}$	12359.66	12359.5362	0.0018	0.0022	1

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[a] D1 and D2 are uncertainties relative to connecting levels and relative to the ground level, respectively, in this Table and in subsequent Tables including D1 and D2. These uncertainties are discussed in the text and fully defined in Kramida (2011). Although occasionally D1 > D2, the level uncertainty with respect to the ground level should be the maximum of D1 or D2. Uncertainties are difficult to evaluate, but are expected to be smaller using interferometric data than older dispersive spectrometer data.

Table 5.
Improved odd parity energy levels of singly-ionized zirconium.

Configuration	Term	J	NIST Levels (cm^{-1})	Levels from UW COGs (cm^{-1})	D1 Uncertainty of Levels from UW COGs (cm^{-1})	D2 Uncertainty of Levels from UW COGs (cm^{-1})	Number of lines connected to level
$4d^2(^3F)5p$	z $^4G°$	$^5/_2$	*27983.83*	*27983.8683*	*0.0006*	*0.0008*	6
		$^7/_2$	*28909.04*	*28908.9353*	*0.0006*	*0.0009*	5
		$^9/_2$	*29839.87*	*29839.8242*	*0.0007*	*0.0011*	4
		$^{11}/_2$	*30795.74*	*30795.6475*	*0.0007*	*0.0013*	2
$4d^2\ (^3F)5p$	z $^2F°$	$^5/_2$	*29504.97*	*29504.9033*	*0.0006*	*0.0008*	6
		$^7/_2$	*30561.75*	*30561.7598*	*0.0006*	*0.0009*	7
$4d^2\ (^3F)5p$	z $^4F°$	$^3/_2$	*29777.60*	*29777.6277*	*0.0006*	*0.0008*	7
		$^5/_2$	*30551.48*	*30551.4717*	*0.0005*	*0.0008*	8
		$^7/_2$	*31249.28*	*31249.2907*	*0.0005*	*0.0010*	6
		$^9/_2$	*31866.49*	*31866.4946*	*0.0007*	*0.0010*	5
$4d^2(^3F)5p$	z $^2D°$	$^3/_2$	*30435.38*	*30435.3065*	*0.0005*	*0.0008*	8
		$^5/_2$	*31160.04*	*31160.0280*	*0.0005*	*0.0008*	9
$4d^2(^3F)5p$	z $^4D°$	$^1/_2$	*31981.25*	*31981.3214*	*0.0009*	*0.0010*	3

	$^{3}/_{2}$	*32256.71*	*32256.7452*	*0.0007*	*0.0008*	6

Table 6 Observed center-of-gravity Zr I transition wavenumbers and Ritz wavenumbers and wavelengths in air organized by increasing wavelength

NIST ASD			this study					
				Observed Center-of-Gravity Transition Wavenumbers (cm^{-1})				
Upper Level[a] (cm^{-1})	Lower Level[a] (cm^{-1})	Ritz wavenumber[a] (cm^{-1})	spectra used[b]	weighted mean[c]	unc.[d]	Ritz Wavenumber (cm^{-1})	unc. (cm^{-1})	Ritz wavelength in air[e] (Å)
26443.88	0.00	26443.88	2,5	26443.7801	0.0026	26443.7802	0.0007	3780.5338
26061.70	0.00	26061.70	2	26061.6942	0.0026	26061.6951	0.0010	3835.9607
25971.71	0.00	25971.71	1,2,5	25971.7262	0.0025	25971.7293	0.0009	3849.2488
26443.88	570.41	25873.47	2	25873.4447	0.0026	25873.4444	0.0007	3863.8712
26342.53	570.41	25772.12	1,2,5	25772.2185	0.0025	25772.2201	0.0009	3879.0475
25729.96	0.00	25729.96	1,2,5	25729.9383	0.0025	25729.9411	0.0007	3885.4216
25630.48	0.00	25630.48	1,2,5	25630.3981	0.0025	25630.3994	0.0010	3900.5119
26765.66	1240.84	25524.82	1,2,5	25524.8650	0.0025	25524.8664	0.0010	3916.6390

Notes

[a] Upper and lower level energies and Ritz wavenumber used to identify transitions are taken from NIST ASD (Kramida et al. 2021)

[b] Numbered as in Table 1

[c] SNR used as weighting factor for calculation of the mean.

[d] Uncertainty estimated from transition SNR and wavenumber calibration uncertainty of spectra contributing to mean

[e] Wavelength in air is calculated from the Ritz wavenumber and the standard index of air from equation 3 of Peck & Reeder (1972)

(This table is available in its entirety in machine readable form in the Supplementary material)

Table 7.
Improved even parity energy levels for neutral zirconium.

Configuration	Term	J	NIST Level (cm^{-1})	Levels from UW COGs (cm^{-1})	D1 Uncertainty of Levels from UW COGs (cm^{-1})	D2 Uncertainty of Levels from UW COGs (cm^{-1})	Number of lines connected to level
$4d^2 5s^2$	a ^{3}F	2	0.00	0.0000	defined	not applicable	23
		3	570.41	570.3358	0.0006	0.0008	26
		4	1240.84	1240.7769	0.0007	0.0009	18
$4d^2 5s^2$	a ^{3}P	2	4186.11	4186.0080	0.0005	0.0008	23
		0	4196.85	4196.7187	0.0009	0.0011	5
		1	4376.28	4376.2441	0.0005	0.0008	20
$4d^3(^4\mathrm{F})5s$	a ^{5}F	1	4870.53	4870.4833	0.0006	0.0008	18
		2	5023.41	5023.3835	0.0004	0.0008	30
		3	5249.07	5249.0696	0.0005	0.0007	29
		4	5540.54	5540.4906	0.0006	0.0008	18
		5	5888.93	5888.8795	0.0009	0.0009	12
$4d^2 5s^2$	a ^{1}D	2	5101.68	5101.6085	0.0005	0.0008	21
$4d^2 5s^2$	a ^{1}G	4	8057.30	8057.2328	0.0010	0.0010	7

$4d^3(^4\mathrm{P})5s$	a ^{5}P	1	10885.36	10885.3361	0.0007	0.0009	8
		2	11016.65	11016.6439	0.0009	0.0009	7
		3	11258.38	11258.3729	0.0006	0.0009	9
$4d^3(^4\mathrm{F})5s$	b ^{3}F	2	11640.72	11640.6485	0.0005	0.0008	13
		3	11956.33	11956.2294	0.0010	0.0009	10
		4	12342.37	12342.2783	0.0007	0.0008	14
$4d^3(^2\mathrm{G})5s$	a ^{3}G	3	12503.44	12503.3346	0.0007	0.0009	7
		4	12760.66	12760.5856	0.0006	0.0008	12
		5	12772.78	12772.6707	0.0008	0.0010	6
$4d^3(\mathrm{b}\ ^2\mathrm{D})5s$	a ^{3}D	1	14123.01	14122.9686	0.0009	0.0012	3
		2	14348.78	14348.7540	0.0008	0.0009	6
		3	14697.03	14696.8984	0.0010	0.0011	3
$4d^3(^2\mathrm{H})5s$	a ^{3}H	4	14791.28	14791.2818	0.0006	0.0009	4
		5	14988.51	14988.4534	0.0008	0.0011	4
		6	15119.66	15119.5818	0.0010	0.0012	3
$4d^3\ (^4\mathrm{P})5s$	b ^{3}P	0	15624.34				
		1	15932.10	15931.9737	0.0007	0.0010	3
		2	16522.23				

$4d^3(^2P)5s$	c ^3P	1	17059.82				
		2	17142.72	17142.5825	0.0009	0.0012	3
		0	17321.52				
$4d^3(^2G)5s$	b ^1G	4	17752.73	17752.6372	0.0006	0.0010	3
$4d^3(^2H)5s$	a ^1H	5	18738.94	18738.9299	0.0011	0.0015	1

Table 8.

Improved odd parity energy levels for neutral zirconium.

Configuration	Term	J	NIST Level (cm^{-1})	Levels from UW COGs (cm^{-1})	D1 Uncertainty of Levels[a] from UW COGs (cm^{-1})	D2 Uncertainty of Levels[a] from UW COGs (cm^{-1})	Number of lines connected to level
$4d^{2}5s5p$	z ^{5}G^{o}	2	*14783.54*	*14783.6563*	*0.0010*	*0.0010*	3
		3	*15201.26*	*15201.3418*	*0.0010*	*0.0009*	4
		4	*15720.36*	*15720.3353*	*0.0009*	*0.0010*	4
		5	*16316.96*	*16316.9587*	*0.0022*	*0.0011*	3
		6	*16978.29*	*16978.2712*	*0.0011*	*0.0015*	1
$4d^{2}5s5p$	z ^{3}F^{o}	2	*16296.51*	*16296.6102*	*0.0007*	*0.0009*	8
		3	*16843.93*	*16843.9911*	*0.0007*	*0.0009*	8
$4d^{2}5s5p$	z ^{5}F^{o}	1	*16786.93*	*16786.9872*	*0.0008*	*0.0011*	3
		2	*17059.61*	*17059.6793*	*0.0006*	*0.0008*	8
		3	*17422.17*	*17422.1794*	*0.0008*	*0.0010*	4
		4	*17832.73*	*17832.7235*	*0.0008*	*0.0011*	4
$4d^{2}5s5p$	z ^{3}D^{o}	1	*17429.86*	*17429.8594*	*0.0006*	*0.0009*	6
		2	*17813.64*	*17813.6602*	*0.0006*	*0.0008*	8
		3	*18243.56*	*18243.5032*	*0.0008*	*0.0009*	10
$4d5s^{2}5p$	z ^{1}D^{o}	2	*17511.78*	*17511.7189*	*0.0008*	*0.0008*	8
$4d^{2}5s(\mathrm{a}\ ^{4}\mathrm{F})5p$	z ^{3}F^{o}	4	*17556.26*	*17556.2452*	*0.0010*	*0.0011*	6

$4d^2 5s(\mathrm{a}\ ^4\mathrm{F})5p$	z $^5\mathrm{F}^\mathrm{o}$	5	*18276.92*	*18276.8972*	*0.0010*	*0.0012*	3
$4d^2 5s5p$	z $^5\mathrm{D}^\mathrm{o}$	0	*18976.36*	*18976.3654*	*0.0014*	*0.0012*	3
		1	*19096.53*	*19096.6397*	*0.0008*	*0.0009*	7
		2	*19323.84*	*19323.9023*	*0.0008*	*0.0010*	6
$4d^2 5s(\mathrm{a}\ ^4\mathrm{F})5p$	z $^5\mathrm{D}^\mathrm{o}$	3	*19625.58*	*19625.6251*	*0.0009*	*0.0009*	6
		4	*19833.78*	*19833.8052*	*0.0012*	*0.0010*	4
$4d^2 5s5p$	z $^3\mathrm{P}^\mathrm{o}$	0	*20233.97*	*20233.9405*	*0.0019*	*0.0015*	2
		2	*20466.83*	*20466.9397*	*0.0009*	*0.0009*	7
		1	*20519.20*	*20519.1552*	*0.0007*	*0.0010*	7
$4d^2 5s5p$	z $^3\mathrm{G}^\mathrm{o}$	3	*21849.33*	*21849.3516*	*0.0005*	*0.0008*	10
		4	*22144.08*	*22144.0078*	*0.0008*	*0.0009*	8
		5	*22563.89*	*22563.8217*	*0.0006*	*0.0009*	8
$4d^2 5s5p$	z $^3\mathrm{S}^\mathrm{o}$	1	*21974.18*	*21974.2190*	*0.0009*	*0.0012*	4
$4d^2 5s5p$	y $^1\mathrm{D}^\mathrm{o}$	2	*22750.53*	*22750.4883*	*0.0010*	*0.0013*	5
$4d^2 5s5p$	y $^3\mathrm{D}^\mathrm{o}$	1	*23018.92*	*23018.8947*	*0.0006*	*0.0009*	9
		2	*23319.86*	*23319.6989*	*0.0006*	*0.0009*	9
		3	*23660.97*	*23660.8691*	*0.0006*	*0.0009*	11
$4d^2 5s5p$	z $^5\mathrm{S}^\mathrm{o}$	2	*23085.06*	*23085.0654*	*0.0008*	*0.0010*	5
$4d^2 5s5p$	y $^5\mathrm{D}^\mathrm{o}$	0	*23122.29*	*23122.2743*	*0.0018*	*0.0021*	1
		1	*23246.33*	*23246.2373*	*0.0012*	*0.0011*	6
		2	*23489.43*	*23489.4289*	*0.0008*	*0.0009*	9

		3	*23889.03*	*23888.9030*	*0.0008*	*0.0009*	11
		4	*24376.37*	*24376.1748*	*0.0010*	*0.0011*	6
$4d^2 5s5p$	y $^3\mathrm{F}^o$	3	*23567.12*	*23567.0759*	*0.0007*	*0.0008*	11
		2	*23597.47*	*23597.4195*	*0.0009*	*0.0009*	11
		4	*24006.30*	*24006.1702*	*0.0010*	*0.0010*	6
$4d^2 5s5p$	y $^1\mathrm{F}^o$	3	*24387.52*	*24387.4642*	*0.0005*	*0.0009*	10
$4d^2 5s5p$	z $^5\mathrm{P}^o$	1	*25489.87*	*25489. 899*	*0.002*	*0.001*	4
		2	*25645.97*	*25646.0536*	*0.0010*	*0.0010*	10
		3	*25898.16*	*25898.2176*	*0.0010*	*0.0009*	11
$4d^3 5p$	y $^5\mathrm{G}^o$	2	*25630.48*	*25630.3994*	*0.0012*	*0.0012*	5
		3	*25971.71*	*25971.7293*	*0.0014*	*0.0011*	7
		4	*26342.53*	*26342.5559*	*0.0009*	*0.0011*	6
$4d^2 5s5p$	y $^3\mathrm{G}^o$	3	*25729.96*	*25729.9411*	*0.0009*	*0.0009*	13
		4	*26011.55*	*26011.4824*	*0.0008*	*0.0009*	10
		5	*26433.72*	*26433.6422*	*0.0008*	*0.0010*	8
$4d^2 5s(\mathrm{a}\ ^2\mathrm{D})5p$	x $^3\mathrm{F}^o$	2	*26061.70*	*26061.6951*	*0.0019*	*0.0012*	6
		3	*26443.88*	*26443.7802*	*0.0013*	*0.0009*	11
		4	*26938.42*				
$4d^3(^4\mathrm{F})5p$	y $^5\mathrm{G}^o$	5	*26765.66*	*26765.6433*	*0.0013*	*0.0012*	6
		6	*27214.89*	*27214.886*	*0.002*	*0.002*	1

Declaration:

None of the three authors have any conflict of interest.

Author Contributions:

The lead author, JEL, conceived of the project, identified the FTS data, and evaluated the Center-of-Gravity for lines with high Signal-to-Noise Ratios. The need for improved energy levels is now more urgent with extremely large telescopes (30 to 50 m diameter primaries) in the design and construction phase. NIST Atomic Spectra Database (ASD) levels are not as accurate as many researchers think. The lead author assumed that the energies levels are accurate to a few times the least significant digit. This is not true and close inspection reveals the accuracy is 25 times the least significant digit. Furthermore, small uncertainties which are now quoted in the ASD are often statistical, and do not include systematic uncertainties unless specified.

The second author, JRS, is an expert in computer software who can invert large matrices and evaluate statistical uncertainties.

The third author, EDH, is PI on the NSF-Astronomy grant which supported this work. She took responsibilities for formatting tables, especially the line-list Tables 2 and 6.

All three authors contributed to writing, editing, and proof reading the manuscript.