First measurement of Lyman alpha x-ray lines in hydrogen-like vanadium: results and implications for precision wavelength metrology and tests of QED

2010 J. Phys. B: At. Mol. Opt. Phys. 43 074021

(http://iopscience.iop.org/0953-4075/43/7/074021)

IOP Publishing Journal of Physics B: Atomic, Molecular and Optical Physics

J. Phys. B: At. Mol. Opt. Phys. **43** (2010) 074021 (9pp) doi:10.1088/0953-4075/43/7/074021

First measurement of Lyman alpha x-ray lines in hydrogen-like vanadium: results and implications for precision wavelength metrology and tests of QED

J D Gillaspy[1], **C T Chantler**[2], **D Paterson**[2,3], **L T Hudson**[1],
F G Serpa[1,4] **and E Takács**[1,5]

[1] National Institute of Standards and Technology, Gaithersburg, MD 20899-8422, USA
[2] University of Melbourne, Parkville, Victoria 3052, Australia

Received 9 September 2009, in final form 30 September 2009
Published 19 March 2010
Online at stacks.iop.org/JPhysB/43/074021

Abstract
The first measurement of hydrogen-like vanadium x-ray Lyman alpha transitions has been made. The measurement was made on an absolute scale, fully independent of atomic structure calculations. Sufficient signal was obtained to reduce the statistical uncertainty to a small fraction of the total uncertainty budget. Potential sources of systematic error due to Doppler shifts were eliminated by performing the measurement on trapped ions. The energies for Ly α_1 (1s-2p$_{3/2}$) and Ly α_2 (1s-2p$_{1/2}$) are found to be 5443.95(25) eV and 5431.10(25) eV, respectively. These results are within approximately 1.5 σ (experimental) of the theoretical values 5443.63 eV and 5430.70 eV. The results are discussed in terms of their relation to the Lamb shift and the development of an x-ray wavelength standard based on a compact source of trapped highly charged ions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In addition to their traditional use for high-temperature plasma diagnostics and as a testbed for fundamental theory, hydrogen-like ions have been proposed as the basis of a calculable x-ray wavelength standard [1, 2] or even as a hyperfine clock frequency standard in the THz to infrared spectral range [3]. Such standards could be disseminated via an electron beam ion trap (EBIT) [4], which provides a relatively compact and affordable source of hydrogen-like ions of arbitrary *Z*. The development of EBITs that fit on a tabletop and operate at room temperatures has been recently reviewed [5]. Before a calculable x-ray standard can be established, however, it is necessary to verify that the spectral lines emitted from the trapped hydrogen-like ions are not significantly perturbed by effects such as satellite line contamination or other potential sources of systematic error.

Although the physics of quantum electrodynamics (QED) underlying the calculations of hydrogen-like V emission is believed to be highly reliable, it is important to test this assumption as well as to check for 'evaluation errors' (mistakes in implementing the known physics). An example of the latter can be found in a recent QED calculation which contributed to the determination of the fine structure constant. When two evaluation errors were discovered in the calculation of 891 Feynman diagrams, a shift in the eighth-order term was 53 times larger than the reported uncertainty, resulting in a 6.5 σ shift in the inferred value of the fine structure constant [6]. Fortunately, no such evaluation errors have been found in the most widely used tabulations of QED results for the

---

[3] Present address: Australian Synchrotron, 800 Blackburn Road, Clayton, Vic 3168, Australia.
[4] Present address: Booz Allen Hamilton, 3811 North Fairfax Drive Suite 600, Arlington, VA 22203-1707.
[5] Present address: University of Debrecen, Experimental Physics Department, Bem tér 18/A, Debrecen, Hungary, H-4026.

energy levels of hydrogen-like ions [7, 8], although some small refinements have been made (see, for example, [9]).

The wavelength measurement we present here is put on an absolute scale by calibrating our spectrometer to external x-ray reference lines which tie back to the primary realization of the unit of length in the metric system [10, 11]. This is in contrast to the more typical method of relying on the calculated wavelengths in hydrogen-like ions to calibrate a spectrometer, then using that spectrometer to measure wavelengths in other ions, and then comparing the results back to the same sort of atomic structure calculation which formed the basis of the calibration in the first place. With a few exceptions, this typical method has been the one that has yielded the prolific results of Beiersdorfer and colleagues at the Lawrence Livermore National Lab (LLNL) EBIT, for example. Because the method essentially uses the experiment as a way of comparing two calculations, it has been dubbed the 'bootstrap method' [12]. Here we demonstrate an absolute calibration, accurate to the 45 parts per million (ppm) level, allowing a fully independent test of atomic structure calculations for the Lyman alpha transitions in H-like V. We believe that our approach can be extended to 12 ppm or beyond with additional effort.

The measurement of wavelengths in highly charged hydrogen-like ions is complementary to wavelength measurements using neutral hydrogen [13], muonium [14–16], positronium [17, 18] and anti-hydrogen [19]. One reason for this is that QED effects scale with a variety of high powers of the ion charge, and even enter with different signs, hence partial cancellations between different terms are varied as one probes a range of nuclear charges and particle masses (see [20] for a discussion of some prominent cancellation errors). Furthermore, a much lower resolution is required to probe the same physics (or to go beyond it) when working with highly charged ions rather than hydrogen, as discussed in more detail below.

The group of T. Hänsch has pushed the spectroscopy of neutral hydrogen to such extremes (1 part in 10^{14}) [13] that it is now two orders of magnitude more accurate than the estimated uncertainty in theory (not including the empirical uncertainty in the proton size). It is expected that many years will be required to extend the theory to much higher precision. An alternative approach is to use nature to enhance the magnitude of some of the small terms that have already been calculated—this can be done by working with H-like ions. The Hänsch group is presently moving from neutral hydrogen to H-like helium ($Z = 2$). Our work presented here is at $Z = 23$. At such a high value of Z, the laser wavelengths needed to probe the low-lying levels are in the x-ray regime. The closest thing to a suitable x-ray laser presently is the linac coherent light source (LCLS) at Stanford [21]. The LCLS, however, must use Bragg crystal monochromators to narrow the bandwidth of the light for use in precision spectroscopy. In our work presented here, rather than using Bragg-narrowed light to excite transitions, we use the Bragg diffraction crystals to analyse the light emitted from ions produced and excited by electron–ion collisions. At $Z = 23$, the first order QED effects scale as Z^4 (giving an enhancement factor of 3×10^5 compared to hydrogen). Of more interest are the higher order terms which scale even more strongly with Z. In the most recent CODATA recommendation for the fundamental constants [22], results on hydrogen are combined with all of the best available QED terms, including terms that scale as Z^7, in order to determine a value for the Rydberg constant at a level of 7 parts in 10^{12}. Scaling these terms up from $Z = 1$ to $Z = 23$ with Z^7 scaling enhances them by a factor of 3×10^9. Relative to the first order terms, which scale as Z^2, the enhancement is 6×10^6.

The terms discussed above, and throughout this paper, are corrections to results which already take into account the effect of relativity to all orders of $Z\alpha$ by using the Dirac equation. It is interesting to note that if one were to try to take relativistic effects into account by applying perturbation theory to the Schrödinger equation, one would need to go to order 22 in powers of $Z\alpha$ (the electromagnetic coupling strength) [10] in order to achieve an accuracy approaching 1 ppm for H-like uranium.

2. Experiment

The present work was preceded by an exploratory experiment carried out at the end of our earlier experiment on helium-like vanadium [23]. A spectrum of some of the raw data from the exploratory experiment was published previously [24], but the energy axis remained in arbitrary units because an investigation of possible sources of systematic error was not complete. Based on our learning from the first experiment, the experiment described here utilized improvements that resulted in higher resolution and improved photon flux. A spectrum of some of the raw (uncalibrated) data for the present experiment was also published in an earlier paper [25]. Here we report the results from this experiment after a thorough calibration was done, including the assessment and correction for a number of systematic errors. These are the first hydrogen-like vanadium Lyman alpha transition wavelengths reported in the literature.

The H-like V ions were produced in the EBIT at the National Institute of Standards and Technology (NIST) [26] under the following conditions. A Helmholtz coil current of 164 A through a superconducting magnet produced a magnetic field of 3.0 T. An electrostatic trap depth of approximately 200 V was produced by the potential on the upper drift tube, while the lower drift tube was held at 500 V. The electron beam current was run at 155 to 183 mA, considerably higher than normal, to boost the signal intensity. Low charge ions from a MEVVA [27] were injected axially at 10 keV and held for 2 s before the beam energy was ramped up to 18 keV over the course of 10 ms and held for an additional 1 s before emptying the trap and starting the injection cycle again. Photons were collected continuously. The beam was centred on the geometric trap axis such that the reflected beam current on the anode and surrounding electrodes was only 0.01% of the injected current. The EBIT base pressure in warm areas was measured to be in the range of 9×10^{-11}–5×10^{-10} hPa, and the pressure in trap centre was undoubtedly much lower due to the surrounding 4.2 K metal surfaces of the drift tubes and magnet.

A beam of nitrogen gas was continuously injected into the trap radially to provide evaporative cooling of the vanadium

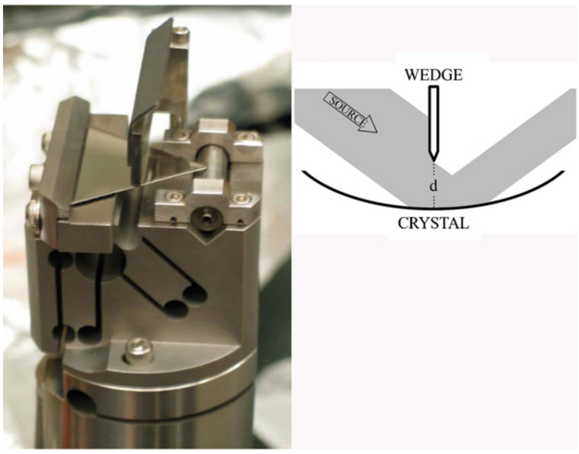

Figure 1. Left: photograph of the triangular crystal mounted in our spectrometer, showing the method used to produce a theoretically perfect cylindrical bend [28]. Right: schematic representation of the Seemann wedge (also visible in the photograph) located at a variable distance *d* above the surface of the crystal.

ions. Because the nitrogen ions have a maximum charge state of 7+ (fully stripped), they experience a shallower electrostatic trap than the V^{22+} ions, and therefore have a lower maximum temperature. The vanadium ions are thus cooled by collisions with the nitrogen ions, shrinking the x-ray source size, improving the overlap with the electron beam and boosting the signal strength. Only a small amount of gas was injected in order to limit the effect of charge exchange and thereby optimize the production of the highest charge states in the trap. The gas was injected through a set of differentially pumped apertures 0.32 cm (1/8″) in diameter, the farthest of which was located 45 cm from the trap centre. The injection pressure behind the farthest aperture was 10^{-7} hPa to 10^{-6} hPa (producing an estimated nitrogen pressure at trap centre of $<10^{-11}$ hPa). The optimum gas injection and other parameters were judged by monitoring the x-rays with a high efficiency lithium-drifted silicon detector; the relative intensity of the hydrogen-like shoulder observed on the helium-like resonance peak with this detector rose to 0.5, indicating an approximately equal population of the two charge states in the trap.

The spectroscopy was performed using x-ray crystal diffraction in the Johann geometry. The crystal was Ge220, 99.999 999% pure, 0.7 mm thick and 270 mm^2 in area, curved to a radius of 1.8 m using the technique described by Henins [28] and shown in figure 1. This technique involves a triangular plate crystal clamped at the base and rotated while the apex (on the right side of the photograph in figure 1) is supported by a freely rotating cylinder, producing a force that is only normal to the local crystal surface. Along the length of the crystal, the linearly increasing bending moment is compensated by the linear increase of the crystal width, theoretically producing perfect cylindrical curvature. This technique removes a major source of systematic error that has limited some of the most precise previous measurements, as described below. Also visible in figure 1 above the centre of the crystal, and illustrated schematically on the right, is the Seemann wedge used to shadow the crystal from the incident x-rays by varying amounts in order to study a number of systematic effects [25].

A backgammon cathode multi-wire proportional chamber was used to detect the x-rays. The crystal, detector and calibration source were located on the Roland circle, and the EBIT was located inside the Roland circle, a configuration that reduces the dependence of the calibration on the exact location of the hydrogen-like ions. The spectrometer was mounted on the NIST EBIT in an orientation that put the Bragg angle in a vertical plane that contained the EBIT electron beam. The angles were referenced to the local gravitational field using arcsecond precision clinometers mounted on the spectrometer arms, the crystal mount and the spectrometer base. Interspersed with our observations of the trapped ions, we made observations of x-ray reference lines by looking directly through the EBIT at solid foil targets of Ti, V, Cr and Mn excited by impact from a second electron beam. Our use of four separate materials provides a wide range of x-ray standards, in comparison to many other measurements which use only one.

3. Analysis and results

In order to put measurements of this sort on an absolute scale from first principles, the crystal lattice spacing and the absolute Bragg angle must be known, and an accurate theory for the x-ray diffraction must be used (a simple application of Bragg's law fails far before the present level of accuracy is reached). The lattice spacing of Ge was determined at NIST by comparison to that of a master silicon crystal (ratio of unit cell dimensions: Ge/Si = 1.041 7570(5) at 22.5 °C [29]), and that of the Si was determined absolutely using a combined x-ray and optical interferometer linked to an iodine-stabilized helium–neon laser and hence tied to the definition of the meter. The effective lattice spacing will change slightly upon curvature, however, and this is taken into account as discussed below.

Many different Bragg angles and crystal curvatures were used in the course of this measurement. The clinometers mounted on the spectrometer allow us to reference the different angles to each other via the local direction of the earth's gravitational field. The absolute value of the angles, as well as small changes in the effective lattice spacing caused by curvature of the crystal, was determined by observing the x-ray reference lines before, after and in the middle of the EBIT observations. Over 100 separate calibration spectra were recorded and analysed to determine the dispersion function. The form of the dispersion function was fixed by dynamical diffraction theory [30], which included the effects discussed below.

In many other experiments on highly charged ions, the measurement accuracy is limited by the statistical uncertainty associated with the weak signal strengths. In the present work, sufficient number of photons were collected so that the statistical uncertainty could be made relatively small, and considerable effort could be put into assessing systematic measurement errors.

Due to an improved application of dynamical diffraction theory in interpreting our data, our vanadium results are more than a factor of two (this paper) to three [23] times more

Table 1. Uncertainty budget for the wavelength determination of the Lyman alpha lines in V.

Contribution	Ly α_1 (1s-2p$_{3/2}$)	Ly α_2 (1s-2p$_{1/2}$)
Dispersion function	40 ppm	40 ppm
Statistical	15 ppm	18 ppm
Reference Lines	12 ppm	12 ppm
Diffraction theory	6 ppm	6 ppm
Temperature	<5 ppm	<5 ppm
Doppler shifts	<4 ppm	<4 ppm
Total	45 ppm	46 ppm

accurate than our previous x-ray work. We believe that much of the other work in this field has not adequately accounted for all of the effects included in such a complete theory, and is therefore compromised at approximately the 100 ppm level [25], corresponding to 10–30% of the Lamb shift in the mid-*Z* range discussed below.

The systematic errors assessed (and adjusted for when appropriate) in the present work include refractive index shifts, geometrical effects such as source shape and position, dependence on Seemann wedge position, crystal mosaicity, asymmetric diffraction, form factor uncertainties, three-beam interactions and crystal d-spacing shifts, detector geometry and position, detector amplitude response linearity and effects due to differential depth penetration and focusing of x-rays in the crystal. Differential depth penetration depends particularly on the dynamical theory of diffraction and is often ignored or overlooked since it cannot be analysed by simple ray tracing. Some of the effects are exacerbated in curved crystal geometries which are often used to increase the signal strength and lower statistical uncertainty. In many cases, failing to use the dynamical theory of diffraction can be the dominant source of error, contributing as much as several hundred ppm to the uncertainty budget [31, 32]. In the present work, all of these sources of systematic error were extensively analysed over the course of several years, using dynamical diffraction theory which combined, for the first time, curvature and mosaicity [31, 32]. More details about the analysis can be found elsewhere [25, 33, 34]. We note that the wavelengths in H-like V are farther from the reference lines than they are in He-like V. This accounts for the fact that the present results are approximately 1.5 times less accurate than our He-like ion results [23]. Our uncertainties are grouped into general categories in the uncertainty budget shown in table 1.

The dominant contribution to the uncertainty is associated with the dispersion function. A variety of effects contribute to this component of uncertainty, including the statistics of the calibration lines (2–10 ppm), the difference of source size and position from trapped ions (20 ppm) and the difference between line peak and centroid (10–20 ppm). The latter can be caused by real structure in the emission spectrum (line blends), but even in the case of purely monochromatic x-rays the effect of differential depth penetration in an absorbing crystal can modify the line shape and shift the centre of the observed line significantly; this effect of dynamical diffraction has been known for decades (see, for example, figure 3–17 of the text by Zachariasen [35]), but is rarely accounted for adequately.

Table 2. Our results, compared to the predictions of Mohr [7] or Johnson and Soff [8].

H-like V	This experiment	Theory [7, 8]	Difference
Ly α_1 (1s-2p$_{3/2}$)	5443.95(25) eV	5443.63 eV	0.32(25) eV
Ly α_2 (1s-2p$_{1/2}$)	5431.10(25) eV	5430.70 eV	0.40(25) eV

The uncertainty of the reference lines is comparable to the statistical uncertainty in our H-like V lines. The absolute accuracy of the standard x-ray reference lines in this region of the spectrum [36] has remained limited to 10 to 15 ppm. Work is currently underway at NIST [37] to produce a new set of reference lines that will greatly exceed this level. In the meantime, we use an adjustment to Bearden's results performed by one of us (CTC). This adjustment shifts the results of Bearden to longer wavelengths by approximately 15 ppm and is somewhat different from the adjustments published by Deslattes *et al* [10]. Our adjustment consists of updating the value of the wavelength standard upon which all of Bearden's numbers hang (the W Kα_1 line). In specific, we convert Bearden's A^* units to absolute units by using the currently most accurate value for the W Kα_1 line [10], resulting in a conversion factor $A^* = 1.000\,015\ A$ [22]. We conservatively retain the original 12 ppm uncertainty of Bearden, rather than using the reduced uncertainty (8–10 ppm) given by Deslattes *et al* [10].

The accurate application of x-ray reference lines can depend on the resolution with which they are observed (due to line asymmetries caused by solid state effects, for example). This is taken into account in our analysis; our resolution is similar to that used by Bearden at Ti K $\beta_{1,3}$ and V Kα, but less at shorter wavelengths. Further details about the analysis presented here can be found in the PhD thesis of one of us [33].

Our results and the associated uncertainties discussed above are given in table 2, where they are compared to theoretical predictions, as discussed in the next section.

4. Comparison to theory

As described in the introduction, the calculations of energy levels in H-like ions [7, 8] are believed to be so highly accurate that they are often used to calibrate spectrometers, and hence the uncertainty of many measurements rests ultimately on the actual accuracy of these calculations. Beiersdorfer has recently [12] reviewed experiments for all values of *Z* that can be used to independently test the calculations since the publication of Johnson and Soff [8], and concluded that experimentalists may have avoided publishing results that differ from these calculations, given that the agreement between the calculations and all published measurements is better than expected from statistical considerations alone. We note that this is known as the 'file drawer problem' in the psychological literature [38]. In the data analysed by Beiersdorfer [12], the typical experiment differs by only about 0.5 σ, with none of 41 plotted measurements differing by more than 1.1 σ. The probability, assuming normal statistics, of 41 independent measurements all falling within 1.1 σ of the prediction by chance alone is approximately 2 parts in one million. Our results presented here differ from the predictions by 1.3 and 1.6 σ. Below, we also discuss some of our previous results that were omitted from the review of Beiersdorfer [12].

Our 45 ppm accuracy of the Lyman energies can be interpreted as a 9% measurement of the 1s-2p$_{3/2}$ and 1s-2p$_{1/2}$ Lamb shifts predicted by QED. These shifts are then found to be 2.35(8)(23) eV and 2.30(10)(23) eV, respectively (the first uncertainty is statistical and the second is systematic). The shifts are defined following Johnson and Soff [8], and do not include the reduced mass shifts. A measurement of similar accuracy ($\approx$35 ppm compared to our $\approx$45 ppm) at $Z = 92$ provides a 1% test of the Lamb shift, currently the most stringent in any highly charged H-like ion [39].

Our results are discussed in terms of the other experiments most similar to ours in section 5 below. In the remainder of this section, we discuss how QED can be used to interpret and scale our results in comparison to those of the most accurate transition energy measurements ever done.

In neutral hydrogen, lasers are available at the appropriate wavelengths needed to probe the transitions, making it possible to test calculations of the Lamb shift down to the current uncertainty in the nuclear size (50 kHz or 6 ppm of the 1 S Lamb shift [40]). Comparing this to our measurement in H-like V requires a consideration of how the various terms that contribute to the Lamb shift scale with nuclear charge. As mentioned in the introduction, some QED terms included in state-of-the-art calculations scale as Z^7, and thus are 3×10^9 times larger in H-like V than in hydrogen. If we scale the uncertainty of our present measurement by Z^{-7}, it corresponds to an absolute accuracy in frequency of 18 kHz, which is 7 parts in 10^{12} of the 1s-2s transition in hydrogen. By coincidence, this is precisely the relative accuracy with which the Rydberg constant is presently known. The much more accurate (34 Hz) measurements in hydrogen from the group of Hänsch are limited in their use for determining the Rydberg constant by the 1 part in 10^{12} uncertainty in theory, and by the even greater uncertainty introduced by the lack of independent knowledge of the nuclear size. Experiments are currently underway to remove the latter uncertainty [14]. Unfortunately, the estimated magnitude of the two-photon QED term that scales as Z^7 discussed above remains too small to be probed by either our experiment or that of Hänsch and colleagues. Recently, however, the Hänsch group has begun working to extend very precise laser techniques to the case of H-like He ions where the B71 term is over 100 times larger.

The limiting accuracy in the theory of the ground state of hydrogen (besides the nuclear size effect) is a particular term describing the exchange of two virtual photons and involving a calculated coefficient known as B60 [22]. The situation involving the B60 term is particularly interesting because calculations in the range $Z = 10$–100 do not extrapolate to the value calculated directly in the limit $Z = 0$. In fact, the slope of the trend calculated for $Z > 10$ would have to reverse sign in the region $Z < 10$ in order to match up with the $Z = 0$ value. The extrapolated value that was available at the time of the last adjustment to the fundamental constants was a full factor of 2 different from the $Z = 0$ value [41]. In contrast, when a similar term (B50) was compared in this way, the agreement was good to within 15% [41]. Because the discrepancy was not understood, the CODATA recommended value at $Z = 1$ was taken as the average of the value extrapolated from $Z > 10$ and that extrapolated from $Z = 0$, with the uncertainty taken as half the difference between the two extrapolations [22]. This resulted in the unusual situation that the Rydberg constant today is slightly less well known than it was in 2002, despite improvements in measurements of transition frequencies in hydrogen (see section IV-A-1-f of [22]). Recent results [42] appear to have reduced the discrepancy in B60 (down from a factor of two to a factor of 1.5, which is marginally consistent with the estimated uncertainties). The B60 term scales as $(Z\alpha)^6$, producing a factor of 10^8 gain at $Z = 23$ (vanadium) compared to hydrogen. The absolute value of the term, however, remains smaller than our experimental uncertainty at $Z = 23$. The examples above illustrate how successful QED has been in accounting for the experimental results in both the low-Z and high-Z regimes, where the relative contributions of the various terms are vastly different. See, however, the discussion by Chantler [43] for a list of some discrepancies and concerns, or see the paper by Chen *et al* [44] for a discussion of the H-like Bi anomaly [45].

Finally, it is interesting to consider how the present results indirectly connect the theoretical results of Mohr [7] or Johnson and Soff [8] for H-like ions to the theoretical results of Drake [46] for He-like ions. The connection comes because many of the tests of Drake's theory are from experiments that use spectrometers calibrated to reference lines from H-like ions, under the assumption that the calculations for the H-like ions are correct. Beiersdorfer [47], for example, has noted a roughly constant offset of approximately 40 ppm between his measurements from $Z = 19$ to 32, and concluded that there is a need to include additional corrections in the calculations. If instead of using the calculations to calibrate the spectrometer, our present measurements were used instead, the offset with Drake would double. A different way of looking at this is that we observe a small offset from the theory of H-like ions that is of similar magnitude and sign as that observed in the case of He-like ions reported by Beiersdorfer [47]. In both cases, however, the offset from any individual measurement is not of sufficient statistical significance to be of great concern.

5. Comparison to previous measurements

The recent review of absolute measurements in H-like ions by Beiersdorfer [12] notes 42 measurements, citing 24 papers (some papers describe multiple measurements). Here we focus on two subsets of these papers: those that involve ions of similar Z and those that were done in an EBIT for any value of Z. We also include some published and unpublished results that were not included in the review by Beiersdorfer [12].

5.1. Comparison to measurements on ions of similar Z

Our results are shown in figure 2, in comparison to other measurements in the range $Z = 17$–36. This figure updates the summary plot in the recent review of Chantler and Kimpton

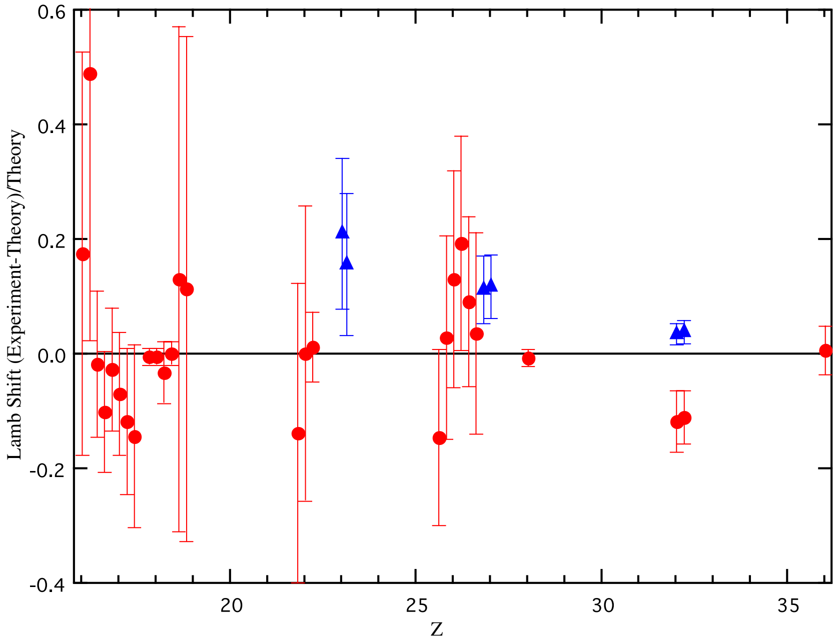

Figure 2. Comparison of other results [49–65] in the mid-Z range to our present results (triangles at $Z = 23$, blue online) and the recent beam-foil results of one of us (triangles at $Z = 26$ [54] and $Z = 32$ [55], blue online) that were not included in the review of Beiersdorfer [12]. Results at the same value of Z are displaced horizontally slightly for clarity. Theory is that of Mohr [7] or Johnson and Soff [8].

[48]. The triangles (blue online) show all of the results published since 2003; these are the results of Chantler and coauthors (including the present results) that use the full dynamical diffraction theory in the analysis [31, 32]. The results shown as (red online) dots at $Z = 32$ are the results of Chantler and coauthors from over 20 years ago [49]), prior to his development of the full dynamical diffraction theory.

The result of Beyer *et al* [50] at $Z = 18$ has the highest previously claimed absolute wavelength accuracy for a H-like ion of any value of Z. The measurement was done on recoil ions produced by an accelerator. The assignment of uncertainty in this experiment merits some scrutiny since no one has been able to exceed it in the intervening 25 years. The uncertainty was limited almost entirely (90%) by line asymmetries caused by satellite contamination. The published raw data show highly asymmetric profiles, and the adjustments that were made by modelling and subtracting a number of satellites of varying widths, positions, and intensities. After subtracting the modelled satellites, the residual profiles were fit to symmetric line shapes to determine the centres, however the fits continued to diverge significantly from the fit profiles beyond the half-width at half-maximum. At two times the half-width at half-maximum, the divergence from the fits was as large as 10%, with the data rising above the fit almost exclusively on the long wavelength side. The linewidths were 70 times wider than the 5 ppm quoted uncertainty in the centres. The actual centres of a symmetric line will be at slightly shorter wavelengths (higher energies) than that determined by the fits to the asymmetric lines. The degree of this shift was minimized by fitting only the data at >40% of the maxima. Even so, the final wavelengths quoted were approximately 5 ppm shorter because in the end the authors concluded that their modelling was not fully adequate, and resorted to simply fitting an arbitrary number of Voigt profiles until the residuals were reduced to the noise level (S/N $\approx$ 30). Seven or more lines were added to the fit, in addition to the H-like lines themselves. The run-to-run variation was as large as 16 ppm, over three times the quoted uncertainty obtained by averaging four runs. The final quoted uncertainty corresponded to an agreement with theory of just under 1 σ (0.9). In a later paper published by the same first two authors (and others) [51], the recoil ion technique used in the earlier paper was described by noting that 'satellite contamination (due to the huge capture cross section) is difficult to keep under control'.

The second most accurate measurement shown in figure 2 (13 ppm) is at $Z = 28$ and was also done by Beyer *et al* [51]. The low uncertainty was obtained despite the fact that the crystal curvature was known to deviate significantly from a uniform cylinder. This contributed to a number of bumps and wiggles in the dispersion curve. The origin of this problem was twofold: (1) the crystal was bent by gluing it to a cylinder, but the glue was found to be thicker in the centre than at the edges, and (2) the back surface of the crystal was ground, rather than polished, leaving significant roughness [66]. The relatively large deviations in the curvature were mapped out using a collimated x-ray source and corrected in the analysis. The crystal used was of the same material and cut as ours (Ge200), but it was bent to nearly a factor of 2 smaller radius. The combined crystal and detector nonuniformity was the main source of uncertainty in this measurement. The shape of the overall dispersion curve was determined by Monte Carlo ray tracing, rather than the dynamical diffraction theory, and only one wavelength standard was used (copper Kα). The lines were curved on the detector by a factor of 4 more than the quoted uncertainty in the detector uniformity, leading to large corrections in this regard also. The agreement with theory suggests that all of these factors (referred to by the authors themselves as 'conspicuous and correctable deficiencies in the experimental arrangements') were handled remarkably well.

The review of Chantler and Kimpton [48] contains a discussion of some of the other potential problems in the experiments summarized in figure 2. The design of our experiment avoids many of these problems from the onset. As described above, however, other problems were then made apparent which limited our final results in the case of H-like V to the 45 ppm level.

5.2. *Comparison to other EBIT measurements*

Experiments on trapped highly charged ions are of particular interest because they are relatively free of Doppler shifts which otherwise often limit the systematic uncertainty in measurements done on highly charged ions. Here, we take a broad view of traps as including not only electron beam ion traps, but also ECRs, Tokamaks and even accelerators (particularly when fed into storage rings)—essentially any experiment in which the ions are held far from material walls in a manner in which the ion velocity (or centre of mass velocity) is under control by the experimenters. Laser-produced plasmas do not generally fit this definition because they are typically created on solid surfaces and move into a hemisphere (or otherwise suffer from motional asymmetries) which leads to Doppler shift uncertainties [67, 68]. Special targets can be manufactured to produce collimated jets from laser-produced plasmas in order to help control the Doppler shifts, but this gain comes at the expense of signal strength [68].

Of the 34 papers reviewed by Beiersdorfer [12], 18 are on accelerators, 2 are on Tokamaks and 4 are on EBITs. Attempts have been made to use ECR ion traps to measure spectra of H-like ions, but to our knowledge these have been unsuccessful due to the relatively low intensities of lines from the highly charged ions in these traps. Accelerator-based experiments are often done on ions moving at nearly the speed of light, in which case large corrections have to be made accurately, or special techniques must be used to slow the ions down after they are created at high velocity. Although Tokamaks are ion traps, their toroidal geometry allows circulatory motion that can lead to systematic Doppler shifts. Satellite line blends are also a problem in Tokamak measurements, and can be even more significant in the final uncertainty budget than Doppler shifts. Both Doppler and satellite shifts are believed to be relatively absent from EBIT experiments, but as detailed below there are only a few ($\approx$4) absolute measurements to directly confirm this.

In fact, the ions inside an EBIT are not exactly at rest. The ion temperature can be 100 000 00 K or more, resulting in a measurable Doppler width [69, 70]. It is often assumed that the centre of mass is at rest, however, so that fits to the peak can be assumed to be free of any net Doppler shift. This is not exactly correct either, however, as the ions may preferentially boil out of the trap in one direction as they are warmed by Spitzer heating from the electron beam. EBIT measurements are often done in an asymmetric axial trap potential to prevent the ions from bombarding the electron gun, and/or to facilitate the collection of extracted ions from the trap, for example. For trap filling times of 1 s (limited, e.g., by the ionization time), this results in a net flow of ions perpendicular to the observation direction of approximately 3 cm s^{-1}—many orders of magnitude smaller than the toroidal velocity in Tokamak experiments [62] or in accelerators. Similarly, asymmetries in the radial trap potential, due to miscentring of the drift tubes in the magnetic field, for example, could give rise to a net flow away from or in the direction of the observation, exacerbated when the trap is operated so as to have a hot ion cloud, but this is expected to be negligibly small.

Beiersdorfer [12] lists only four previous measurements on an EBIT which provide absolute values for the H-like transitions. One of the four depends subtly on a theoretical calculation of the binding energy, and therefore bears some discussion. Unlike the other measurements, this fourth one [71] is based on radiative recombination (RR) rather than transitions between two bound states. The use of RR for precision spectroscopy is possible in an EBIT because the electron beam energy is sharply peaked, providing a pool of initial electron energies which has a spread that is small compared to the technical uncertainty in a bound electron's energy (limited by the spectrometer resolution). Hence, RR appears as 'lines' in an EBIT experiment. The measured energy is the sum of the atomic ionization energy and the electron beam energy. The latter is not precisely known or calculable due to space charge shifts in the trap, but it can be measured by simultaneously recording a RR line in another ion for which the binding energy has been independently determined. The difference in the RR line energies then gives the difference in the binding energies. Unfortunately, in the EBIT RR experiment [71], only a transition energy between two levels of the second ion was known, not the absolute value of the binding energy. Hence, a calculation for the binding energy of a higher-lying level in the second ion was used to obtain a value for the binding energy of the first ion. This result was then compared to the same sort of calculation that was used to obtain the upper level of the reference line. The experiment can then either be interpreted as a theory-dependent 120 ppm measurement of the binding energy of H-like Rh or as a 330 ppm absolute measurement of the difference between the binding energies of the ground states of H-like Rh and H-like Kr. The theory-dependent interpretation emphasized in the original publication is of value because high-lying levels in lower mass ions have smaller QED corrections. For leading order terms that scale as Z^4 and $1/n^3$, the corrections are smaller by a factor of nearly 20.

As figures of merit for comparing various measurement accuracies, we can consider the energy of the transition (E), the absolute uncertainty of the energy (ΔE), the relative uncertainty of the energy ($\Delta E/E$), the relative uncertainty in the Lamb shift determination (ΔE/QED) and the nuclear charge (Z). These quantities for the present experiment are compared to those in other absolute measurements of the Lyman alpha transitions in hydrogen-like ions trapped with

Table 3. Some figures of merit for various absolute measurements of Ly α_1 transitions in hydrogen-like ions trapped in an EBIT.

Ly α_1 (1s-2p$_{3/2}$)	LLNL1 [72]	LLNL2 [73]	Oxford [58]	Present work
E	1.5 keV	2.0 keV	5.0 keV	5.4 keV
ΔE	0.035 eV	0.14 eV	0.14 eV	0.25 eV
$\Delta E/E$	24 ppm	71 ppm	28 ppm	45 ppm
ΔE/QED	12%	28%	6%	9%
Z	12	14	22	23

Table 4. Some figures of merit for various absolute measurements of Ly α_2 transitions in hydrogen-like ions trapped in an EBIT.

Ly α_2 (1s-2p$_{1/2}$)	LLNL1 [72]	LLNL2 [73]	Oxford [58]	Present work
E	1.5 keV	2.0 keV	–	5.4 keV
ΔE	0.071 eV	0.21 eV	–	0.25 eV
$\Delta E/E$	48 ppm	107 ppm	–	45 ppm
ΔE/QED	25%	44%	–	9%
Z	12	14	–	23

essentially no net centre of mass motion in tables 3 and 4. In this table we use the tabulated values of the Lamb shift from Johnson & Soff [8], which do not include the reduced mass terms.

Less data are available for the transition to the first excited state (table 4), and most of that is substantially less accurate than the data for the transition to the next highest excited state (table 3), at least partly because the former transition has half the intensity of the latter. Our results are roughly equally accurate in both cases because our signals are strong enough that counting statistics are only a minor limitation on our final uncertainty. Compared to the other available absolute measurements done with an EBIT, ours is at the highest Z and therefore the highest transition energy, and for the transition to the first excited state (Ly α_2) ours has the lowest fractional uncertainty in both the total energy and in the Lamb shift.

6. Conclusions

Despite the fact that our measurements were carried out in a way that removes a number of factors that have limited the best previous measurements (such as nonuniformities in crystal curvature, lack of statistics, satellite and Doppler shifts), our use of an extraordinarily rigorous application of dynamical diffraction theory to check for consistency with a wide range of x-ray wavelength standards have revealed other uncertainties, such as those associated with the predicted diffraction line shape, that limit our results to approximately 45 ppm in the case of the Lyman alpha transitions in H-like V. We believe our results will be extensible to 12 ppm or beyond. We recommend that future work that seeks to exceed the level of accuracy of several tens of ppm take into full account the systematic effects that we describe, and that claims to go beyond this without doing so perhaps should be considered with caution.

Acknowledgments

We thank Peter Mohr, Paul Indelicato, Albert Henins and Kevin Coakley for useful discussions, Vladimir Yerokhin for sharing his work in advance of publication and Mark Kinnane for the schematic diagram on the right side of figure 1 (from his doctoral dissertation at the University of Melbourne). The present work was supported by the Australian Research Council.

References

[1] Flowers J L, Klein H A and Margolis H S 2004 *Contemp. Phys.* **45** 123

[2] Anagnostopoulos D F, Gotta D, Indelicato P and Simons L M 2003 *Phys. Rev. Lett.* **91** 240801

[3] Schiller S 2007 *Phys. Rev. Lett.* **98** 180801

[4] Levine M A, Marrs R E, Henderson J R, Knapp D A and Schneider M B 1988 *Phys. Scr.* **T22** 157

[5] Zschornack G, Kreller M, Ovsyannikov V P, Grossman F, Kentsch U, Schmidt M, Ullmann F and Heller R 2008 *Rev. Sci. Instrum.* **79** 02A703

[6] Gabrielse G, Hanneke D, Kinoshita T, Nio M and Odom B 2007 *Phys. Rev. Lett.* **99** 039902

[7] Mohr P J 1983 *At. Data Nucl. Data Tables* **29** 453

[8] Johnson W R and Soff G 1985 *At. Data Nucl. Data Tables* **33** 405

[9] Mohr P J and Soff G 1993 *Phys. Rev. Lett.* **70** 158

[10] Deslattes R D, Kessler E G, Indelicato P and Lindroth E 2006 *International Tables for Crystallography* vol C, ed E Prince (Berlin: Springer) ch 4.2.2C, p 200

[11] Deslattes R D, Kessler E G, Indelicato P, de Billy L, Lindroth E and Anton J 2003 *Rev. Mod. Phys.* **75** 35

[12] Beiersdorfer P 2009 *Can. J. Phys.* **87** 9

[13] Fischer M *et al* 2004 *Phys. Rev. Lett.* **92** 230802

[14] Nebel T *et al* 2007 *Can. J. Phys.* **85** 469

[15] Maas F E *et al* 1994 *Phys. Lett.* A **187** 247

[16] Chu S, Mills A P, Yodh A G, Nagamine K, Miyake Y and Kuga T 1988 *Phys. Rev. Lett.* **60** 101

[17] Fee M S, Mills A P, Chu S, Shaw E D, Danzmann K, Chichester R J and Zuckerman D M 1993 *Phys. Rev. Lett.* **70** 1397

[18] Chu S, Mills A P and Hall J L 1984 *Phys. Rev. Lett.* **52** 1689

[19] Gabrielse G *et al* 2004 *Phys. Rev. Lett.* **93** 073401

[20] Cheng K T, Chen M H, Johnson W R and Sapirstein J 2008 *Can. J. Phys.* **86** 33

[21] Bozek J D 2009 *Eur. Phys. J. Spec. Top.* **169** 129

[22] Mohr P J, Taylor B N and Newell D B 2008 *Rev. Mod. Phys.* **80** 633

[23] Chantler C T, Paterson D, Hudson L T, Serpa F G, Gillaspy J D and Takács E 2000 *Phys. Rev.* A **62** 042501

[24] Chantler C T, Paterson D, Hudson L T, Serpa F G, Gillaspy J D and Deslattes R D 1997 *Phys. Scr.* **T73** 87
[25] Chantler C T, Paterson D, Hudson L T, Serpa F G, Gillaspy J D and Takács E 1999 *Phys. Scr.* **T80B** 440
[26] Gillaspy J D 1997 *Phys. Scr.* **T71** 99
[27] Brown I G, Galvin J E, Gavin B F and Macgill R A 1986 *Rev. Sci. Instrum.* **57** 1069
[28] Henins A 1987 *Rev. Sci. Instrum.* **58** 1173
[29] Henins A 2009 Private communication
[30] Chantler C T and Deslattes R D 1995 *Rev. Sci. Instrum.* **66** 5123
[31] Chantler C T 1992 *J. Appl. Crystallogr.* **25** 674
[32] Chantler C T 1992 *J. Appl. Crystallogr.* **25** 694
[33] Paterson D 1999 *PhD Thesis* University of Melbourne
[34] Paterson D, Chantler C T, Hudson L T, Serpa F G, Gillaspy J D and Takács E 2001 Absolute test of quantum electrodynamics for helium-like vanadium *The Hydrogen Atom: Precision Physics of Simple Atomic Systems* (Berlin: Springer)
[35] Zachariasen W H 1945 *Theory of X-ray Diffraction in Crystals* (London: Wiley)
[36] Bearden J A 1967 *Rev. Mod. Phys.* **39** 78
[37] Kinnane M N and Hudson L T 2009 Private communication
[38] Rosenthal R 1979 *Psychol. Bull.* **86** 638
[39] Gumberidze A *et al* 2005 *Phys. Rev. Lett.* **94** 223001
[40] Yerokhin V A, Indelicato P and Shabaev V M 2005 *Nucl. Instrum. Methods Phys. Res.* B **235** 36
[41] Yerokhin V A, Indelicato P and Shabaev V M 2005 *Phys. Rev.* A **71** 040101
[42] Yerokhin V A 2009 *Phys. Rev.* A **80** 040501 (R)
[43] Chantler C T 2004 *Radiat. Phys. Chem.* **71** 611
[44] Sapirstein J and Cheng K T 2008 *Can. J. Phys.* **86** 25
[45] Klaft I *et al* 1994 *Phys. Rev. Lett.* **73** 2425
[46] Drake G W 1988 *Can. J. Phys.* **66** 586
[47] Beiersdorfer P, Bitter M, Vongoeler S and Hill K W 1989 *Phys. Rev.* A **40** 150
[48] Chantler C T and Kimpton J A 2009 *Can. J. Phys.* **87** 763
[49] Laming J M, Chantler C T, Silver J D, Dietrich D D, Finch E C, Mokler P H and Rosner S D 1988 *Nucl. Instrum. Methods Phys. Res.* B **31** 21
[50] Beyer H F, Deslattes R D, Folkmann F and Lavilla R E 1985 *J. Phys. B: At. Mol. Phys.* **18** 207
[51] Beyer H F, Indelicato P, Finlayson K D, Liesen D and Deslattes R D 1991 *Phys. Rev.* A **43** 223
[52] Briand J P, Mosse J P, Indelicato P, Chevallier P, Girardvernhet D, Chetioui A, Ramos M T and Desclaux J P 1983 *Phys. Rev.* A **28** 1413
[53] Briand J P, Tavernier M, Indelicato P, Marrus R and Gould H 1983 *Phys. Rev. Lett.* **50** 832
[54] Chantler C T, Laming J M, Dietrich D D, Hallett W A, McDonald R and Silver J D 2007 *Phys. Rev.* A **76** 042116
[55] Chantler C T, Laming J M, Silver J D, Dietrich D D, Mokler P H, Finch E C and Rosner S D 2009 *Phys. Rev.* A **80** 022508
[56] Deslattes R D, Schuch R and Justiniano E 1985 *Phys. Rev.* A **32** 1911
[57] Richard P, Stöckli M, Deslattes R D, Cowan P, Lavilla R E, Johnson B, Jones K, Meron M, Mann R and Schartner K 1984 *Phys. Rev.* A **29** 2939
[58] Tarbutt M R and Silver J D 2002 *J. Phys. B: At. Mol. Opt. Phys.* **35** 1467
[59] Tavernier M, Briand J P, Indelicato P, Liesen D and Richard P 1985 *J. Phys. B: At. Mol. Phys.* **18** L327
[60] Dohmann H D, Liesen D and Pfeng E 1983 *GSI Sci. Rep.* 155
[61] McClelland A F 1989 *Thesis* Oxford University
[62] Källne E, Käällne J, Richard P and Stöckli M 1984 *J. Phys. B: At. Mol. Phys.* **17** L115
[63] Marmar E S, Rice J E, Källne E, Källne J and Lavilla R E 1986 *Phys. Rev.* A **33** 774
[64] Silver J D, McClelland A F, Laming J M, Rosner S D, Chandler G C, Dietrich D D and Egan P O 1987 *Phys. Rev.* A **36** 1515
[65] Schleinkofer L, Bell F, Betz H D, Trollmann G and Rothermel J 1982 *Phys. Scr.* **25** 917
[66] Indelicato P 2009 Private communication
[67] Reader J 2009 *Phys. Scr.* **T134** 014023
[68] Herbst M J, Burkhalter P G, Grun J, Whitlock R R and Fink M 1982 *Rev. Sci. Instrum.* **53** 1418
[69] Beiersdorfer P, Decaux V and Widmann K 1995 *Nucl. Instrum. Methods Phys. Res.* B **98** 566
[70] Adler H, Meyer E S, Serpa F G, Takács E, Gillaspy J D, Brown C M and Feldman U 1995 *Nucl. Instrum. Methods Phys. Res.* B **98** 581
[71] Nakamura N, Nakahara T and Ohtani S 2003 *J. Phys. Soc. Japan* **72** 1650
[72] Hölzer G, Förster E, Klöpfel D, Beiersdorfer P, Brown G V, López-Urrutia J R C and Widmann K 1998 *Phys. Rev.* A **57** 945
[73] Tschischgale J, Klöpfel D, Beiersdorfer P, Brown G V, Förster E, Schulte-Schrepping H and Utter S B 2002 *Can. J. Phys.* **80** 867