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High-Precision Transition Energy Measurements of Neonlike Fe XVII Ions

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ABSTRACT

We improve eight-fold the energy accuracy of the strongest soft X-ray transitions of Fe XVII ions by resonantly exciting them in an electron beam ion trap with a monochromatic beam at the P04 beamline of the PETRA III synchrotron facility. By simultaneously tracking instantaneous photon-energy fluctuations with a high-resolution photoelectron spectrometer, we minimize systematic uncertainties down to velocity-equivalent $\pm \sim 5$ km/s in their rest energies, substantially improving our knowledge of this key astrophysical ion. Our large-scale configuration-interaction computations include more than four million configurations and agree with the experiment at a level without precedent for a ten-electron system. Thereby, theoretical uncertainties for interelectronic correlations become far smaller than those of quantum electrodynamics (QED) corrections. The present QED benchmark strengthens our trust in future calculations of many other complex atomic ions of interest to astrophysics, plasma physics, and for the development of optical clocks with highly charged ions.

1. INTRODUCTION

Over the past three decades, extensive research has focused on the soft X-ray emission from Ne-like iron (Fe XVII, Fe¹⁶⁺), particularly in hot astrophysical plasmas observed by *Chandra* and *XMM-Newton* (Behar et al. 2001; Brinkman et al. 2001). The dominant spectral transitions $3d \rightarrow 2p$ and $3s \rightarrow 2p$ of Fe XVII within the 14.5 to 17 Å range play a crucial role in deducing the plasma parameters across various sources. These parameters include electron temperature, density, elemental abundance, gas motion, and photon scattering opacity (Parkinson 1973; Smith et al. 1985; Schmelz et al.

1992; Waljeski et al. 1994; Phillips et al. 1996; Behar et al. 2001; Mauche et al. 2001; Doron & Behar 2002; Xu et al. 2002; Gu 2003; Paerels & Kahn 2003; Werner et al. 2009; Pradhan & Nahar 2011; Beiersdorfer et al. 2018; Gu et al. 2019, 2020; Grell et al. 2021).

Despite decades of study, since early solar X-ray observations (Parkinson 1973; Smith et al. 1985; Schmelz et al. 1992; Waljeski et al. 1994), discrepancies between observed and theoretical intensity ratios (Brown et al. 1998) have persisted. Early explanations invoking resonance scattering (McKenzie et al. 1980; Schmelz et al. 1992; Saba et al. 1999) found no confirmation in measurements with electron beam ion traps (EBITs) and tokamaks that also agreed with solar observations (Brown et al. 1998, 2001a,b; Brown et al. 2006; Beiersdorfer et al. 2002; Gillaspay et al. 2011; Beiersdorfer et al. 2004; Beiersdorfer et al. 2017; Shah et al. 2019). As op-

tically thin laboratory plasmas are not subject to resonance scattering, indirect line formation mechanisms were suggested (Chen & Pradhan 2002; Gu 2003; Beiersdorfer et al. 2008, 2014, 2015; Shah et al. 2019; Grilo et al. 2021; Gu et al. 2020). An experiment with a free-electron laser aimed at directly determining the oscillator-strength ratio for lines 3C and 3D without uncertainties due to electron-impact excitation. Its unexpected results departing even more from theory were attributed to inaccuracies in calculated oscillator strengths (Bernitt et al. 2012), but soon after, unforeseen transient non-equilibrium effects and population transfer due to the ultra-brilliant peak photon flux explained them (Oreshkina et al. 2014, 2016; Loch et al. 2015; Wu & Gao 2019). Our later measurements (Kühn et al. 2020) with synchrotron radiation avoided this non-linear systematic and improved the accuracy of the oscillator strength ratio while still disagreeing with theory. Finally, further increases in resolving power and signal-to-noise ratio found the cause of the persistent discrepancies in hitherto unresolvable line wings and diffraction effects, and brought the oscillator-strength ratio in line with state-of-the-art predictions (Kühn et al. 2022).

In spite of these advances, many questions remain open for this essential ion and many other less-studied species. For instance, widely used wavelength references for Fe XVII from EBIT measurements using a crystal spectrometer with a resolving power of 500–700 have uncertainties that are Doppler-equivalent to ~ 50 km/s, i.e. ~ 180 parts-per-million (ppm), for $n = 3 - 2$, and double that for high- n transitions (Beiersdorfer & Wargelin 1994; Brown et al. 1998). This is only marginally adequate for analysis of high resolution diffraction grating spectra acquired with the *Chandra* High Energy Transmission Grating Spectrometer (HETGS), which can measure velocities of bright emission lines with 25 km/s systematic uncertainty (Ishibashi et al. 2006; Bozzo et al. 2023). These uncertainties in transition energies will also impair achievement of the science goals of other extant, upcoming, and proposed missions, including *XMM-Newton* (Jansen et al. 2001; den Herder et al. 2001), *XRISM* (Tashiro et al. 2018), *Athena* (Pajot et al. 2018; Barret et al. 2016), *LEM* (Kraft et al. 2022), *Arcus* (Heilmann et al. 2022; Smith et al. 2022), and *Lynx* (Schwartz et al. 2019). Furthermore, comparing these best available measurements to the large number of published calculations (Loch et al. 2005; Aggarwal et al. 2003; Liang & Badnell 2010) shows differences of up to 500–1000 km/s, demonstrating that widely used theoretical methods cannot provide sufficiently accurate transition energies for more complex multielectron ions. There is clearly a need for better determinations of the Fe XVII transition energies that will allow us to take full advantage of the resolving power of current and future missions, as well as improved and well-benchmarked theoretical methods that

can provide energies for transitions which have not yet been measured with sufficient precision.

We report new measurements of the rest energies of key Fe XVII transitions with an EBIT at the P04 beamline of the PETRA III synchrotron with uncertainties below 15 ppm, an eight-fold improvement over the status quo. Our results translate in velocity terms to 5 km/s, and fully unlock the value of archived and forthcoming observations from *XMM-Newton* and *Chandra*, as well as of accurate velocimetry targeted by upcoming missions (Pajot et al. 2018; Barret et al. 2016; Kraft et al. 2022; Heilmann et al. 2022; Smith et al. 2022). We also test the large-scale configuration interaction (CI) approach and, therefore, our combination of the CI and coupled-cluster approaches (CI+all-order method), crucial for the development of high-precision clocks (Kozlov et al. 2018), and essential for understanding quantum electrodynamics (QED) effects in many-electron system. By applying the model potential approach (Tupitsyn et al. 2016) using the QEDMOD package (Shabaev et al. 2018), we incorporate QED effects into the effective Hamiltonian, basis-set orbitals, and one-electron matrix elements—a widely employed practice. The quality of the QED model potential is usually assessed against exact solutions for H-like ions, since the uncertainty in the electronic correlation in HCI with a few valence electrons is usually larger, or at the level of QED contributions, unless the ionization degree is rather high. Until this work, there were no estimates regarding the accuracy of QEDMOD approach for the majority of many-electron systems.

Motivated by our highly-accurate experimental results, we carry out new CI computations, taking into account contributions from high nl states, increasing the number of configurations from 1.2 million in our previous work (Kühn et al. 2022; Cheung et al. 2021) to over 4 million, and investigating the convergence of the computations in both of these parameters. The results show a remarkable degree of numerical convergence across all energy levels, and agree with the measurements to a level of 2–40 ppm that is unprecedented for a complex ion such as Fe XVII. For the first time, uncertainties in the electronic correlations smaller than QED corrections allow us to test the accuracy of the QED contribution in a many-electron system.

2. MEASUREMENTS AND DATA ANALYSIS

PolarX-EBIT (Mücke et al. 2018) was designed for the study of highly charged ions interacting with X-ray photons at synchrotrons and free-electron lasers (see Leutenegger et al. 2020; Togawa et al. 2020; Kühn et al. 2020; Kühn et al. 2022; Steinbrügge et al. 2022; Stierhof et al. 2022). Its off-axis electron gun emits a nearly monoenergetic electron beam that is compressed to a diameter of less than 100 μm by a magnetic field of 870 mT generated by permanent magnets.

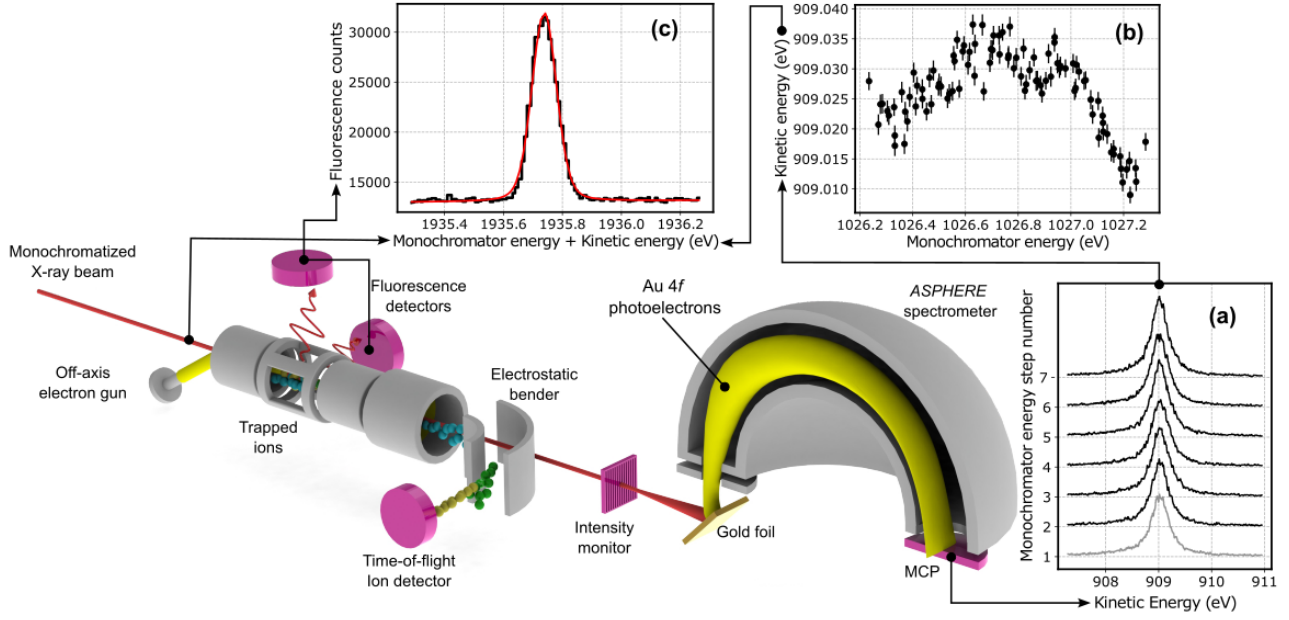


Figure 1. A photon beam of variable energy excites an elongated ion ensemble within a portable electron beam ion trap, PolarX-EBIT (Micke et al. 2018). Emitted fluorescence X-rays are recorded by two silicon drift detectors. Ions periodically released from the trap are mass-analyzed by their time-of-flight as a monitoring diagnostic of the trapped ion content. Downstream, the photon beam passes through a wire mesh used to measure its intensity before hitting a gold target and releasing photoelectrons that enter ASPHERE, a high-resolution hemispherical electron-energy analyzer, which records (a) the Voigt-like kinetic energy distribution of Au 4f_{7/2} electrons and its centroids (b) at each monochromator energy step. This reveals small, but reproducible periodic deviations from the, nominally linear, monochromator energy scale that are corrected for (c) prior to calibration with reference lines.

Considering the overlap of the ion cloud and the electron beam leads to an effective electron density of $\sim 10^{10} \text{ cm}^{-3}$. Iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) molecules enter the trap region as tenuous beam through a two-stage differential pumping system. There, electron impact dissociation generates Fe atoms, and step-wise electron-impact ionization produces highly charged ions that remain radially trapped by the ensuing negative space-charge potential of the electron beam, and axially by biased cylindrical drift tubes. We chose operating conditions to ensure that Fe XVII ions mostly populate the trap.

At the soft X-ray beamline P04, an APPLE II undulator (Viefhaus et al. 2013) produces circularly polarized photons, which are then sent through a monochromator equipped with a variable line-spacing grating of 1200 lines/mm mean groove density. Using an exit slit opening of 50 μm , the energy resolution ΔE was set to a value of approximately $E/\Delta E \approx 13,000$ in the energy range of 700 to 1100 eV. A pair of plane-elliptical mirrors refocuses this beam onto the ion cloud. The photon beam energy is scanned over the Fe XVII transitions of interest and the corresponding calibration lines. Two silicon drift detectors (SDD) mounted at the top and on the side of the EBIT register fluorescence following from resonant photoexcitation as well as electron-impact excitation.

To calibrate the monochromator energy scale, we excite K-shell transitions in H-like and He-like oxygen, fluorine,

and neon ions trapped in PolarX-EBIT. Their energies can be calculated with uncertainties well below 1 meV. We take values for the H-like $1s \rightarrow 2p$ transitions from Yerokhin & Shabaev (2015), and from Erickson (1977) for $1s \rightarrow np$ up to $n = 7$, and for He-like ions, we take energy values from Yerokhin & Surzhykov (2019) for $1s - np$ transitions up to $n = 7$.

The monochromator disperses the spectrum of the undulator cone on the exit slit by choice of incidence and diffraction angles of the grating, which is accomplished by appropriate rotations of both the grating and mirror, with the extra degree of freedom removed by requiring fulfillment of the constant fix-focus (CFF) condition (Follath 2001). The absolute angles of both grating and mirror are recorded using angular encoders. To measure electronic transitions with narrow natural line widths $< 50 \text{ meV}$, angular increments as small as $\approx 10^{-5}$ degrees have to be resolved, equivalent to 36 milliarcsseconds or 175 nrad. The installed encoders have 36 000 reference marks per turn, or one every 10^{-2} degrees. Their readout is therefore interpolated, making them prone to periodic subdivision errors.

This problem was previously observed in our studies at P04 (Kühn et al. 2022; Togawa et al. 2023) and other beamlines (Follath & Balzer 2010; Krempaský et al. 2011), and leads to periodic fluctuations around the nominal photon-energy scale, which in our case have peak-to-peak amplitudes

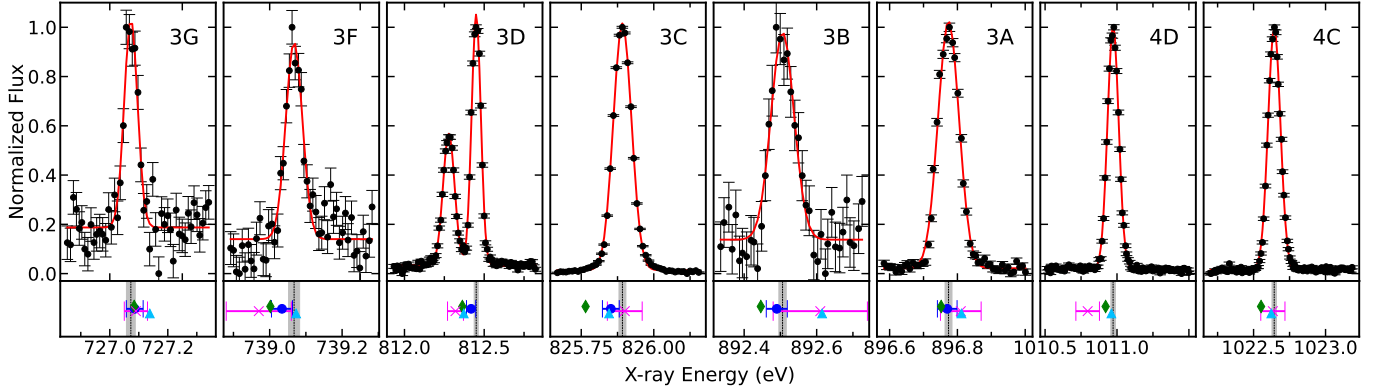


Figure 2. (Top) Individually measured soft X-ray transitions of Fe XVII. (Bottom) Measured transition energies (grey band) vs. Large CI (blue circles), MBPT (green diamonds), previous laboratory data (magenta crosses), and solar observations (cyan triangles).

of up to ~ 50 meV below 900 eV and ~ 70 meV above 900 eV. To correct for them while scanning the monochromator to excite resonant transitions, we direct the photon beam exiting the EBIT onto a gold target mounted on a high-resolution hemispherical electron-energy analyzer, ASPHERE (Rossnagel et al. 2001), as shown in Fig. 1. There, $4f_{5/2,7/2}$ photoelectrons are emitted, and their kinetic energy measured. By changing the bias potential of the gold target in par with the nominal photon energy, the photoelectron peaks should appear at fixed positions on the electron detector. Any deviation from the nominal value would result in changes in kinetic energy, as displayed in Fig. 1 (b). The variable bias ensures that the stronger peak (Au $4f_{7/2}$) remains centered on the detector, see Fig. 1 (a). We fit these peaks (linewidths of about 700 meV FWHM) with Voigt profiles to find their centroids and determine their kinetic energies with uncertainties of a few meV at electron count rates of $\sim 10^4$ /s. By cooling the gold target to liquid nitrogen temperature, we further reduce the peak width to ~ 450 meV, which further improves centroid determination. We use this information to correct the nominal monochromator energy scale at each step, see Fig. 1 (b). We then determine the centroids of the calibration lines on the corrected scale (Fig. 1 (c)), associate them with the theoretical references mentioned above, and fit the dispersion curve over the range 650 to 1150 eV with a third-order polynomial.

For the Fe XVII measurements we set the EBIT to use a ~ 4 mA, 3500 eV electron beam, capable of directly exciting the lines studied here, and thus generating an undesired background. These parameters yielded a ratio of photoexcitation peak to electron-impact background between 2 and 3 throughout the experiment, indeed lower than the ratio of ≈ 45 achieved in our previous work (Kühn et al. 2022) by cyclically switching the electron-beam energy between ion breeding and probing energy after a long parameter optimization. This time, since switching tests showed a severe loss of Fe XVII ions, we decided to use a constant energy of 3500 eV, well above that of dielectronic recombination satellites. The

present signal-to-noise ratio and resolving power of 13 000 were sufficient for our reported accuracy.

The P04 monochromator was scanned over ranges covering $3s - 2p$ (3G and 3F), $3d - 2p$ (3C and 3D), $3p - 2s$ (3A and 3B), and $4d - 2p$ transitions (4C and 4D) of Fe XVII. Fluorescence was collected for 10–15 s at each monochromator step. The count rate for each transition is directly proportional to the respective oscillator strength, and we can see transitions with excitation rates about 4–80 times lower than that of the 3C transition. Scans of each line were therefore repeated as needed to obtain good statistics. This also yielded adequate statistics at each step for the Au $4f_{7/2}$ photoelectron peak position determination needed for the photon-energy scale correction. A representative scan for each of these lines is shown in Fig. 2. To determine the centroids of the Fe XVII lines, we fit Voigt profiles with a Gaussian component reflecting the Doppler width of the trapped ions and the apparatus profile of the monochromator (Hoesch et al. 2022). The Lorentzian contribution, as shown in (Kühn et al. 2022), arises from both the natural linewidth of the transitions and a pseudo-Lorentzian instrumental component caused by X-ray diffraction at beamline elements.

Table 1 presents the results for eight Fe XVII lines and their associated uncertainties from errors in centroid determination of calibration lines, the dispersion fit $1-\sigma$ confidence band, and the centroid determination of each Fe XVII line, which is typically in the range of 1–3 meV. The total systematic uncertainties of the calibration are estimated to reach levels of 10–15 meV. As mentioned before, the angular encoder interpolation error induces oscillations of the photon energy scale up to ± 70 meV in the 650–1150 eV energy range. While accurate reference energies and the corrections from ASPHERE to the photon energy axis help mitigating these oscillations, ~ 10 –20% residual variations still remain. A potential source of these could be the limited resolution of the Keithley 6517 voltage source biasing the gold target. Despite using a 7-digit calibrated voltmeter (Agilent 3458a), the voltage source operates in 5 mV steps within the

Table 1. Experimental results and calculations of this work in comparison with previous experiments, astrophysical observations, and other predictions. Values in parentheses following the measured values give total uncertainties and parentheses below the measured values indicate absolute differences from the present measurements.

Line	Term	Configuration	Experiment	This Work		Other Experiments/Observations		
				Large CI ^a	FAC-MBPT ^b	LLNL-EBIT ^c	Hinode ^d	SMM ^e
3G	³ P ₁	[1s ² 2s _{1/2} ² 2p _{1/2} ² 2p _{3/2} ³ 3s _{1/2}] ₁	727.073(15)	727.086 (-0.013)	727.084 (-0.011)	727.09(4) (-0.02)	727.14 (-0.06)	727.14 (-0.06)
3F	¹ P ₁	[1s ² 2s _{1/2} ² 2p _{1/2} ² 2p _{3/2} ⁴ 3s _{1/2}] ₁	739.067(15)	739.034 (0.033)	739.002 (0.065)	738.97(9) (0.10)	739.07 (-0.01)	739.10 (-0.03)
3D	³ D ₁	[1s ² 2s _{1/2} ² 2p _{1/2} ² 2p _{3/2} ³ 3d _{5/2}] ₁	812.417(13)	812.418 (-0.001)	812.363 (0.054)	812.32(5) (0.10)	812.37 (0.05)	812.74 (-0.33)
3C	¹ P ₁	[1s ² 2s _{1/2} ² 2p _{1/2} ² 2p _{3/2} ⁴ 3d _{3/2}] ₁	825.870(12)	825.852 (0.018)	825.765 (0.106)	825.90(6) (-0.03)	825.85 (0.02)	825.90 (-0.03)
3B	³ P ₁	[1s ² 2s _{1/2} ² 2p _{1/2} ² 2p _{3/2} ⁶ 3p _{1/2}] ₁	892.496(10)	892.490 (0.006)	892.446 (0.050)	892.61(13) (-0.11)	892.61 (-0.12)	892.61 (-0.12)
3A	¹ P ₁	[1s ² 2s _{1/2} ² 2p _{1/2} ² 2p _{3/2} ⁶ 3p _{3/2}] ₁	896.774(10)	896.770 (0.004)	896.752 (0.022)	896.81(6) (-0.04)	896.81 (-0.04)	896.88 (-0.10)
4D	³ D ₁	[1s ² 2s _{1/2} ² 2p _{1/2} ² 2p _{3/2} ³ 4d _{5/2}] ₁	1010.983(16)	-	1010.921 (0.062)	1010.80(8) (0.19)	1010.96 (0.02)	1011.04 (-0.06)
4C	¹ P ₁	[1s ² 2s _{1/2} ² 2p _{1/2} ² 2p _{3/2} ⁴ 4d _{3/2}] ₁	1022.639(16)	-	1022.552 (0.087)	1022.63(8) (0.01)	1022.62 (0.02)	1022.80 (-0.16)

^a Large CI calculations, method is from [Cheung et al. \(2021\)](#)

^b CI + Second-order MBPT of FAC, method is from [Gu et al. \(2006\)](#); [Gu \(2003\)](#)

^c Weighted mean and error of measurements from [Brown et al. \(1998\)](#) and [Beiersdorfer & Wargelin \(1994\)](#), as was done in [Beiersdorfer et al. \(2017\)](#), except for 4C and 4D values which are from [Brown et al. \(1998\)](#).

^d Solar Observations by *Hinode*: [Del Zanna & Ishikawa \(2009\)](#)

^e Solar Observations by *SMM*: [Phillips et al. \(1982\)](#)

100 V range, limiting our electron kinetic energy measurements. Further systematics arise from the frequent switching of the voltage range of this bias supply needed to cover the monochromator range of 600 – 1150 eV, requiring separate calibration for each voltage range. Unfortunately, we could only calibrate the bias supply in a narrow 20-V range. Moreover, unmeasured fluctuations in the voltages applied to the inner and outer hemispheres of the electron spectrometer may have introduced additional systematic uncertainties. The dimensional stability of its electron-optics components is affected by thermal drifts caused by varying ambient conditions at ppm levels to which we are already sensitive. After conservatively considering all these sources, our present uncertainties are a factor of 8 smaller than those of previously reported experiments ([Beiersdorfer & Wargelin 1994](#); [Brown et al. 1998](#)).

3. DISCUSSION OF THE RESULTS

We compare the present results in Fig. 2 and Tabs. 1, 2 with earlier experimental data, observations, and predictions, including our own. Our calculations employ the latest version of our highly scalable parallel CI code ([Cheung et al. 2021](#))

(see Appendix). Optimization of the basis set construction allowed faster convergence with the principal quantum number n than in our prior work (*c.f.* supplementary material of [Kühn et al. \(2022\)](#)), while including higher partial waves (h , i , and k), and larger number of reference configurations of even and odd parity. Table 3 shows the QED and other contributions in cm⁻¹ for the measured transitions. Column 17g shows the results obtained with the 17spdfg basis set (see the Appendix); column > 17g, additional contributions from highly excited orbitals up to 24spdfgh21i17k; “Extras”, additional contributions due to the much larger number of configurations included in CI, selected to give the large contributions. The final results are the sum of these three columns and a QED contribution ([Tupitsyn et al. 2016](#)). Columns ΔExp. show differences between the current experiment and theory, and ΔExp.^a show differences from previous calculations presented in ([Kühn et al. 2022](#)), demonstrating a significant improvement. We estimate the uncertainty in the electronic correlation computations to be approximately 230 cm⁻¹, primarily arising from the > 17g contribution (see Appendix). The difference between theory and experiment is within the combined uncertainties for all six levels. This allows us to es-

Table 2. Table 1 continued...

Line	Large CI ^f (old)	Exp. ^g	NIST ASD ^h	AtomDB ⁱ CI	CHIANTI ^j MRMP	CHIANTI ^k AS	SPEX ^l	W16 ^m MBPT	S15 ⁿ MBPT	G05 ^o MBPT	A04 ^p MCDF
3G	726.97 (0.10)	727.11 (-0.03)	727.14 (-0.07)	725.79 (1.28)	727.06 (0.01)	727.48 (-0.41)	727.18 (-0.11)	726.78 (0.29)	-	727.12 (-0.05)	725.38 (1.70)
3F	738.91 (0.16)	739.04 (0.03)	739.05 (0.01)	738.01 (1.06)	739.00 (0.07)	738.21 (0.85)	738.88 (0.19)	738.72 (0.34)	-	739.06 (0.01)	736.05 (3.02)
3D	812.32 (0.10)	812.41 (0.01)	812.37 (0.05)	811.70 (0.72)	812.41 (0.01)	813.65 (-1.23)	812.48 (-0.06)	812.04 (0.37)	812.57 (-0.15)	812.44 (-0.02)	811.08 (1.34)
3C	825.76 (0.11)	825.83 (0.04)	825.70 (0.17)	825.83 (0.04)	825.76 (0.11)	827.52 (-1.65)	826.01 (-0.14)	825.39 (0.48)	825.89 (-0.02)	825.70 (0.17)	825.01 (0.86)
3B	-	-	892.50 (-0.00)	894.25 (-1.75)	892.41 (0.08)	895.55 (-3.05)	892.61 (-0.12)	892.21 (0.29)	-	892.40 (0.10)	894.25 (-1.75)
3A	-	-	896.90 (-0.13)	898.54 (-1.77)	896.67 (0.10)	899.85 (-3.08)	897.14 (-0.36)	896.46 (0.31)	-	896.62 (0.15)	898.55 (-1.77)
4D	-	-	1011.00 (-0.02)	1009.79 (1.19)	-	1012.03 (-1.05)	1011.29 (-0.31)	1010.53 (0.46)	-	-	1009.22 (1.76)
4C	-	-	1022.70 (-0.06)	1021.76 (0.88)	-	1023.64 (-1.00)	1022.97 (-0.33)	1022.17 (0.47)	-	-	1020.90 (1.74)

^f Large CI: [Kühn et al. \(2022\)](#)^g Private Communication [Kramida \(2019\)](#)^h NIST Atomic Spectroscopy Database: [Kramida et al. \(2022\)](#)ⁱ AtomDB Database: [Loch et al. \(2006\)](#) (APED: `fe_17_LV_v3_0_4_a.fits`)^j Chianti Database with MRMP calculations: [Del Zanna & Ishikawa \(2009\)](#)^k Chianti Database with Autostructure (AS) calculations: [Liang & Badnell \(2010\)](#)^l SPEX database: [Gu et al. \(2020\)](#)^m MBPT by [Wang et al. \(2016\)](#)ⁿ MBPT by [Santana et al. \(2015\)](#)^o MBPT by [Gu \(2005\)](#)^p MCDF by [Aggarwal et al. \(2003\)](#)

timite the uncertainty of the QED contribution at 240 - 260 cm^{-1} , which is the combined theory and experimental uncertainties added in quadrature. We also computed the energies of the 3A and 3B levels for the first time. The $2s - 3p$ lines (3A and 3B), which involve a $2s$ electron, have the largest QED contributions ($\sim 3000 \text{ cm}^{-1}$), while for $3s - 2p$ transitions 3G and 3F as well as $3d - 2p$ ones (3C and 3D) they are much smaller. From the 3A and 3B results, we thus estimate a relative QED accuracy of 8%.

As shown in Tab. 1, line 3F, close to the F-K α calibration line, shows a larger absolute deviation of about 33 meV from the large CI prediction, while the remaining measured lines remain below ~ 10 – 20 meV. Unfortunately, line 3F was measured only once, unlike the others, which were scanned at least 4–5 times. We explored several plausible explanations for the 3F discrepancy. One possible source of the discrepancy could be the simultaneous excitation of high n Rydberg lines of O VII within the scan range of line 3F, which could

lead to a shift of the 3F centroid. Furthermore, we considered lines from the lower charge states, Fe X, Fe VIII, and Fe VII, which fall within the 3F scan range. Despite the relatively low abundance of these charge states in our experiment, they can potentially influence the 3F line due to their strong oscillator strengths. Although the theoretical line positions and oscillator strengths of these low charge states are calculated by [Gu et al. 2006](#), they have never been compared experimentally, making it difficult to estimate their influence on the 3F position. We also investigated the possibility of magnetically induced mixing of the $J = 0$ and $J = 1$ ($2p_{1/2}^{-1} 3s_{1/2}$) excited states ([Beiersdorfer et al. 2003](#)), which might shift the energy of the $J = 1$ state sufficiently to introduce a systematic error in our measurement of 3F. However, measurements by [Beiersdorfer et al. \(2016\)](#) show a separation of ~ 1.2 eV between these states, making strong magnetic-field-induced mixing unlikely. We performed FAC calculations for atoms in strong magnetic fields to verify this,

Table 3. Contributions to the theoretical energies (in cm^{-1} above the ground state) of Fe XVII from an enlarged basis set ($> 17g$), additional reference configurations (Extras) and QED in comparison with our measurements and their errors in cm^{-1} .

	Level		This Exp.	Error	$\Delta\text{Exp.}^a$	17g	$> 17g$	Extras	QED	Final	$\Delta\text{This Exp.}$	$\Delta\text{This Exp.} (%)$
3G	$2s^2 2p^5 3s$	1	5864236	121	836	5862842	541	146	814	5864343	-107	0.002%
3F	$2s^2 2p^5 3s$	1	5960974	121	1272	5958941	558	146	1067	5960711	263	0.004%
3F-3G			96738		436	96099	17	0	253	96368	370	
3D	$2s^2 2p^5 3d$	$^3D_1^o$	6552582	105	782	6552044	294	104	151	6552594	-12	-0.0002%
3C	$2s^2 2p^5 3d$	$^1P_1^o$	6661088	97	892	6660390	248	5	299	6660942	145	0.002%
3C-3D			108506		110	108346	-46	-99	148	108348	157	
3B	$2s 2p^6 3p$	$^3P_1^o$	7198462	81		7200865	573	-28	-2993	7198416	46	0.001%
3A	$2s 2p^6 3p$	$^1P_1^o$	7232967	81		7235357	547	-8	-2958	7232938	28	0.0004%
3A-3B			34505			34492	-25	20	35	34522	-17	

^a This column shows the difference of previous theoretical large CI computations from Kühn et al. (2022) with present experiment.

finding shifts on the order of 10 μeV for the field strength in PolarX-EBIT, demonstrating that this effect is not important in our experiment. Moreover, the decrease in reflectivity of the platinum-coated diffraction grating over the 3F scan range could slightly affect the centroid position determination at 739 eV. Based on simulations we estimate this effect to be smaller than 0.1 meV.

We also consider the differences of the three line pairs, as they are more sensitive to QED effects than absolute energies. Table 3 shows that the largest uncertainty, caused by the uncertainty in the basis-set convergence, is common to each of the pairs. This significantly reduces the uncertainty of electronic correlations to better than 50 cm^{-1} for the energy difference. Both (3A-3B) and (3C-3D) are in excellent agreement with our predictions. For (3G-3F), the deviation is about 2σ and can be attributed to the factors discussed above for the line 3F. It is interesting to note that our measured 3F energy is in much better agreement with solar observations (Phillips et al. 1982; Del Zanna & Ishikawa 2009) than with our calculations. Nevertheless, our present calculations show an order of magnitude smaller deviation from our experimental results compared to our prior predictions (Kühn et al. 2022). This represents a benchmark with our experimental data at the level of 10–20 ppm, an unprecedented agreement for a neonlike system to the best of our knowledge.

Besides CI, we performed calculations using a combination of conventional CI and second-order many-body perturbation theory (MBPT) with the Flexible Atomic Code (FAC) (Gu 2008). Details of this method are documented in Gu (2005); Gu et al. (2006). We now include frequency-dependent Breit interactions in both the CI expansion and the MBPT corrections, as well as self-energy and vacuum polarization calculated using the QED operator model of Shabaev et al. (2018). These predictions demonstrate a reasonable agreement with our experimental data, with the largest dis-

crepancy of about 100 meV observed for line 3C. We compared our results with other CI+MBPT data available in the literature (Wang et al. 2016; Santana et al. 2015; Gu 2005). These comparisons showed maximum deviations of up to 0.5 eV, and departures from multi-configuration Dirac-Fock (MCDHF) predictions (Aggarwal et al. 2003) reaching as high as 1–3 eV.

Other accurate predictions for Fe XVII from multi-reference Møller-Plesset (MRMP) are reported in Del Zanna & Ishikawa (2009) and included in the CHIANTI code. They show very good agreement with our experimental data. Notably, FAC-MBPT and MRMP values have their largest deviations from line 3C, but appear in close agreement with the experimental results from Brown et al. (1998). Usage of the experimental value of 3C as reference to assess the convergence of their calculations could perhaps explain this finding.

We also compared our results with the hitherto best laboratory data from Brown et al. (1998). They used a crystal spectrometer and the Lawrence Livermore National Laboratory (LLNL) EBIT. Discrepancies for lines 3F, 3C, and 4D could be due to contamination from the simultaneous trapping of fluorine ions for calibration. Since 3F is close to line w of F VIII, and 3C is to line $\text{Ly}\alpha$ of F IX, their spectral overlap could have affected both the positions and the intensity ratios of the transitions, as discussed in detail in Beiersdorfer et al. (2017). Comparing the values reported by Brown et al. (1998) with those of Beiersdorfer & Wargelin (1994) also shows clear deviations, although both measurements used a similar spectrometer and set of calibration lines. To address this, as in Beiersdorfer et al. (2017), we took a weighted average of both LLNL measurements, and compared it with our data, finding better agreement, especially for lines 3C and 3F. However, the average of 3D disagreed more than the single value from Brown et al. (1998). The likely cause is an unresolvable blend of the Fe XVI satellite C and Fe XVII 3D in

the crystal spectrometer, which did not reach the required resolving power of at least 8000, which we amply surpass in our experiment. By considering the measured energy of line 3D in the crystal spectrometer data as the centroid value for the blend 3D/C, we could infer the real energy of line 3D in those works, reducing the departure from our present measurements of 3D from 100 meV to 50 meV. For this, we took into account the separation between lines 3D and C (≈ 170 meV) measured in this work, their oscillator strengths, and the Fe XVI/Fe XVII population.

The noticeable difference of line 4D could be due to contamination, or the lack of a nearby calibration line. Nevertheless, solar observations by the Hinode (Del Zanna & Ishikawa 2009) and SMM (Solar Maximum Mission) (Phillips et al. 1982) missions show a better agreement with our experiment for the lines 3F and 4D than with previous laboratory studies. Because the solar abundance of fluorine is very low, those observations are less affected by that contaminant. The data from both agree very well with our experiment, except for lines 3B and 3D, the latter being affected by the line C blend. Part of the differences between our measurements and those at the LLNL EBIT result could be from improved calibration references. For example, a difference in F Ly α energy of 100 meV between the Garcia & Mack (1965) reference used by Brown et al. (1998) and the one from Yerokhin & Shabaev (2015) used here.

We also compare our results with data from widely used databases and plasma codes. The NIST Atomic Spectroscopy Database (ASD) (Kramida et al. 2022) values showed significant deviations for lines 3C and 3A. However, when critically evaluated $n = 3 - 2$ data by the authors of the NIST ASD (Kramida 2019) were considered, we found a much better agreement with our experimental results, see Tab. 2. Comparison with AtomDB (Foster et al. 2012), CHIANTI (Del Zanna et al. 2021), and SPEX (Kaastra et al. 1996) databases and plasma codes revealed discrepancies as large as 1–2 eV. SPEX numbers showed better agreement with our results than those found in AtomDB, since SPEX has updated Fe-L atomic data (Gu et al. 2019, 2020, 2022), which were mainly calculated using FAC. Although the Astrophysical Plasma Emission Database (APED) version in AtomDB shows different values in its online webguide version (2.0.1)¹ and its pyatomdb version (3.0.4), the theoretical source is in both cases Loch et al. (2005), which uses the CI method, and disagrees by up to 1–2 eV from our results, as shown in Tab. 2. CHIANTI provides two sources for the energies: Autostructure (AS) theory (Liang & Badnell 2010), and the more accurate set of data from MRMP theory (Del Zanna & Ishikawa 2009). Note that source of the energy data in-

side these models/databases and resulting model spectrum using these databases have some differences. For examples, the AtomDB model inside XSPEC uses the observed energies by Brown et al. (1998), whereas CHIANTI uses the observed transition energies from solar Observation (Del Zanna & Ishikawa 2009).

Overall, most experimental and observational data agree with our experiment within 0.1 eV on average, well within error bars of earlier works. However, there are substantial discrepancies with predictions from certain theoretical models, exceeding the margins of error associated with the experimental results. This highlights the urgent need to update the aforementioned databases to avoid pitfalls in astrophysical spectrum modeling and interpretation of observational data.

4. SUMMARY AND CONCLUSIONS

We presented high-precision transition-energy measurements of eight strong, astrophysically preeminent Fe XVII transitions required for plasma diagnostics. Our approach combined resonant photoexcitation of Fe XVII and narrow H-like and He-like transitions with high-resolution photoelectron spectroscopy (Rossmagel et al. 2001). This eliminates a very common source of systematic errors found even in advanced monochromators, namely quasi-periodic encoder interpolation errors (Follath & Balzer 2010; Krempaský et al. 2011). As a result, our Fe XVII measurements are the most accurate to date, improving on older experimental references by almost an order of magnitude, with uncertainties equivalent to Doppler shifts of $\approx \pm 5$ km/s. A further improvement in accuracy by another order of magnitude will require incorporating high-resolution/-stability voltage sources and more accurate voltmeters at ASPHERE to eliminate systematic errors associated with knowledge of the bias voltages.

We have also improved our high-precision calculations by an order of magnitude in comparison with previous best calculations (Kühn et al. 2022; Cheung et al. 2021). This improvement allowed us, for the first time, to test the accuracy of QED corrections to the transition energies of a complicated 10-electron system. We expect that the achieved QED accuracy is applicable to a broad range of ions of intermediate degrees of ionization that can be treated with our large-scale CI or CI+all-order approaches. This has significant implications for predicting energy levels in systems where no experimental data are available for a wide range of applications in astrophysics, plasma physics, and atomic clocks development (King et al. 2022). The established QED accuracy is deemed sufficient for high-precision prediction of HCI clock transitions (Kozlov et al. 2018). Improved accuracy of the experimental values would allow to further decouple uncertainty due to basis-set convergence from the uncertainty in the QED and improve theory predictions.

¹ <http://www.atomdb.org/Webguide/webguide.php>

Our improved transition energy measurements for Fe XVII are sufficiently accurate that the uncertainties are no longer a significant part of the error budget for present or future planned astrophysical instruments, such as *Chandra* HETGS, *XMM-Newton* RGS, *XRISM* (Tashiro et al. 2018), *Athena* (Pajot et al. 2018), *LEM* (Kraft et al. 2022), *HUBS* (Cui et al. 2020), *Arcus* (Heilmann et al. 2022), *HiReX* (Nicastro et al. 2021), and *Lynx* (Schwartz et al. 2019). Future campaigns of similar measurements of prominent transitions in key ions (especially Fe L-shell ions) would be of great utility and could easily be directly included in commonly used astrophysical plasma spectral databases.

The closeness of our large CI calculations to our measured values, with the worst deviation (line 3F) amounting to a Doppler shift of only 13 km/s, shows that such well-converged calculations are sufficiently accurate to be readily used in spectral databases. While there is no reason for this in the case of the lines measured in the present work, when accurate measurements are not available, similarly well-converged results could be used for other transitions of Fe XVII and many other ions. By including a very large number of configurations, our agreement becomes significantly better than that of other well-performing methods, such as results from less-converged large CI, MBPT and MRMP calculations. For Fe XVII, our calculations are more accurate than even the best measurements for Fe L-shell transitions in

Li-like through F-like ions (Brown et al. 2002). This suggests a near-future research program composed of comprehensive large-CI calculations of transition energies for all ions of astrophysical interest up to Ne-like, supplemented by targeted experiments aimed at measuring the most important transition energies.

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APPENDIX

A. LARGE-SCALE CI CALCULATIONS

In this work, we conducted extensive high-precision calculations of Fe XVII. We start from the solution of the Dirac-Hartree-Fock equations in the central field approximation to construct the one-particle orbitals. Calculations are carried out using a CI method, correlating all 10 electrons. Breit interaction is included in all calculations. QED corrections are taken from the previous work (Kühn et al. 2022) except for the levels with a 2s hole, which were not computed in 2022. The same method is used in all QED calculations (Tupitsyn et al. 2016). The CI wave function is obtained as a linear combination of all distinct states of a given angular momentum J and parity:

$$\Psi_J = \sum_i c_i \Phi_i. \quad (\text{A1})$$

The low-lying energies and wave functions are determined by solving the time-independent multi-electron Schrödinger equation

$$H\Phi_n = E_n\Phi_n. \quad (\text{A2})$$

Expanding the previous work (Kühn et al. 2022), we perform several calculations optimizing the basis set convergence, including higher partial waves up to k orbitals, and significantly expanding the set of reference configurations until convergence is reached in these parameters as well.

We have shown a comparison of our theoretical results for six transitions measured in this work with the experiment in the main text. We note that such a larger scale computation of the 4C and 4D levels is beyond the capabilities of available computational resources (32 TB of memory and about 2000 CPUs on our largest available partition). Computing higher-lying levels requires computing of all the lower lying levels with the same angular momentum and parity, drastically increasing memory requirement.

To test the consistency of our approach, we compare the data for the even and larger number of odd levels in Tab. 4 with Kramida (2019). These experimental data re-analyzed by Kramida (2019) generally agree well with our experiment (except for levels with a 2s hole), so they serve as a good general reference for other levels. The six levels measured in this work are shown

Table 4. Contributions to Fe XVII energies calculated with increased basis sets and number of configurations. The results are compared with the experiment from [Kramida \(2019\)](#). All energies are given in cm^{-1} . The basis set is designated by the highest principal quantum number and the highest partial wave included. For example, 17g means that all orbitals up to $n = 17$ are included for *spdfg* partial waves. The last two columns show the differences of the present computations with [Kramida \(2019\)](#) in cm^{-1} and %, respectively.

Configuration	Expt ^a	Δ Ref. ^b	17g	+20g	+24g	+17h	+20h	+24h	+17i	+21i	+17k	QED	Extras	Final	Δ	$\Delta(\%)$ Present	
$2s^2 2p^6$	1S_0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
$2s^2 2p^5 3p$	3S_1	6093295	1124	6092365	44	20	278	58	45	64	86	8	70	107	6093143	152	0.002%
$2s^2 2p^5 3p$	3D_2	6121484	988	6120688	38	18	252	51	40	56	77	4	56		6121280	204	0.003%
$2s^2 2p^5 3p$	3D_3	6134539	1015	6133678	41	19	258	54	42	58	81	5	107		6134345	194	0.003%
$2s^2 2p^5 3p$	1P_1	6143639	1013	6142785	39	18	253	52	40	56	78	4	93		6143417	222	0.004%
$2s^2 2p^5 3s$	2	5849216	1134	5847527	38	16	269	52	35	63	81	8	813	149	5849052	164	0.003%
$2s^2 2p^5 3s$	1	5864502	1102	5862842	37	15	258	50	34	60	81	7	814	146	5864343	158	0.003%
$2s^2 2p^5 3s$	1	5960742	1040	5958941	41	18	259	55	37	60	81	7	1067	146	5960711	31	0.001%
$2s^2 2p^5 3d$	$^3P_1^o$	6471640	1148	6470765	51	24	138	65	47	22	81	-2	95	139	6471426	214	0.003%
$2s^2 2p^5 3d$	$^3P_2^o$	6486183	1007	6485436	51	24	121	65	47	17	81	-4	109	139	6486086	97	0.001%
$2s^2 2p^5 3d$	$^3F_4^o$	6486720	920	6486064	51	24	90	65	47	7	81	-7	105	142	6486669	51	0.001%
$2s^2 2p^5 3d$	$^3F_3^o$	6492651	856	6492060	50	23	66	64	46	-2	81	-10	102	138	6492621	30	0.000%
$2s^2 2p^5 3d$	$^1D_2^o$	6506537	855	6505941	50	23	62	64	46	-3	81	-10	107	138	6506500	37	0.001%
$2s^2 2p^5 3d$	$^3D_3^o$	6515203	807	6514654	50	23	49	63	46	-8	81	-12	107	136	6515189	14	0.000%
$2s^2 2p^5 3d$	$^3D_1^o$	6552503	703	6552044	51	24	49	65	47	-9	81	-12	151	104	6552594	91	0.001%
$2s^2 2p^5 3d$	$^3F_2^o$	6594309	802	6593569	55	26	71	69	50	0	81	-9	355	138	6594404	95	0.001%
$2s^2 2p^5 3d$	$^3D_2^o$	6600998	938	6600124	54	26	80	69	49	2	81	-8	349	137	6600962	36	0.001%
$2s^2 2p^5 3d$	$^1F_3^o$	6605185	857	6604381	54	26	56	69	49	-6	81	-11	363	136	6605198	13	0.000%
$2s^2 2p^5 3d$	$^1P_1^o$	6660770	574	6660390	54	26	11	68	49	-23	81	-17	299	5	6660942	172	0.003%
$2s 2p^6 3p$	$^3P_1^o$	7199200		7200865	47	30	248	56	38	65	81	8	-2993	-28	7198416	784	0.011%
$2s 2p^6 3p$	$^3P_2^o$			7219595	48	31	251	57	39	66	81	8	-2944	-36	7217197		
$2s 2p^6 3p$	$^1P_1^o$	7233292		7235357	46	30	235	54	35	61	81	6	-2958	-8	7232938	354	0.005%

^a Kramida (2019)

^b Kühn et al. (2022). This column shows the difference of previous theoretical large CI computations from Kühn et al. (2022) with experiment by Kramida (2019).

in bold. The final values are given in cm^{-1} in Tab. 4 in the column “Final”. The difference between the final values and the experimental values in cm^{-1} and percentage are given in the last two columns.

We will discuss a complete assessment of the main contributions to the energies, including the basis set construction, the inclusion of extra configurations, and QED. We find excellent agreement with experiments for all energies, at the level of 0.0004% for some levels. With the high level of accuracy attained, we are able to test QED contributions in the calculations of multi-electron systems for the first time.

Computation — We consider Fe XVII as a system with 10 valence electrons and start with all possible single and double excitations to any orbital up to 17*spdfg* from the $1s^2 2s^2 2p^6$ and $1s^2 2s^2 2p^5 3p$ even basic configurations, and the $1s^2 2s^2 2p^5 3s$, $1s^2 2s^2 2p^5 3d$ and $1s^2 2s 2p^6 3p$ odd basic configurations. We designate the basis set by the highest principal quantum number and the highest partial wave included. For example, 17g means that all orbitals up to $n = 17$ are included for *spdfg* partial waves. Note that $1s^2$ is removed from all the designations to save space.

The base calculation for the energy levels is done with a 17g basis set and is listed in cm^{-1} in Tab. 4 in column “17g”. The contributions to the energy levels from expanding the basis set to 20g and 24g are in the columns “+20g” and “+24g”, respectively. The largest difference between the 23g and 24g calculations was 3 cm^{-1} , so the basis set at the level of *spdfg* partial waves is considered sufficiently saturated. We note that although the 24*spdfg* basis was also used in Kühn et al. (2022), we constructed more compact basis in the present work, to significantly improve convergences with the principal quantum number n . The basis is constructed in the 5 a.u. cavity, while the basis in Kühn et al. (2022) was constructed in a 20 a.u. cavity, with additional differences in the constructions of the higher partial wave orbitals. Detailed comparison of the two computations confirms much better convergence properties of the present basis. We note very large computational resources needed for a basis set expansion, especially for the inclusion of higher partial waves.

Contributions to higher partial waves are considered in the next six columns of Tab. 4. We calculated the contributions of extending the base 17g basis set to include up to 17h orbitals and list them in column “+17h”. Next, we successively increase the principal quantum number and increase the basis set up to 24h. The contributions from (18–20)h orbitals and (21–24)h

orbitals are given in columns “+20*h*” and “+24*h*”, respectively. The largest difference between 23*h* and 24*h* calculations was 9 cm⁻¹, so the energies of including the higher *h* orbitals have also converged sufficiently. We note that a large fraction of the *nh* contribution comes from very high *n* orbitals, so inclusion of the first few *h* orbitals does not give correct results for this partial wave. This effect is exacerbated for the *i* and *k* orbitals, where more of the contribution is expected to come from *n* > 20 even with the present compact basis.

The same procedure was used to obtain contributions from the *i* orbitals up to 21*i* and *k* orbitals up to 17*k* and are listed under columns “+21*i*” and “+17*k*”, respectively. Contributions from including *i* orbitals up to the same principal quantum number *n* = 17 as the base run are listed in column “+17*i*”. Due to the high computational demand for higher partial-wave calculations, we did not perform calculations for odd-parity states at the level of 21*i*. Instead, we set the contributions of 21*i* to the odd-parity energies to be the average of the even-parity state contributions, which was 81 cm⁻¹. Contributions from *k* orbitals were already at a level of convergence around 15 cm⁻¹ at 21*i*.

We note that we have performed detailed convergence studies computing a separate contribution for each *nl* for the last few principal quantum numbers to evaluate convergence. Based on these data, we conservatively estimate the missing higher *g* orbital contribution at 5 cm⁻¹, higher *h* orbital contribution at 20 cm⁻¹, and higher *i* orbital contribution at 50 cm⁻¹. It appears that 17*k* is not sufficiently converged. Table 4 shows that the contribution of all *ni* orbitals is about 1/2 of the *nh* contribution. Conservatively assuming a similar convergence pattern for higher partial waves gives 70 cm⁻¹ for the *k* partial wave and a similar total contribution for all the other partial waves. The total uncertainty due to the convergence of the basis set is then of the order of 230 cm⁻¹. However, we note that the incomplete convergence of the basis is expected to cause a systematic shift of data for all levels. i.e. all energy values will be larger, with some smaller variances between the levels. It is possible that the partial wave convergence is faster and the overall shift is smaller; therefore, we only use the above estimate to make an accuracy evaluation, but do not shift the theory values. We note that overall +100 cm⁻¹ shift of all of our values would improve the agreement of our data with the present experiment, however, this is the level of the experimental precision at 1 σ so improved experimental precision is needed to definitively test the basis set convergence.

Additionally, an extensive evaluation of the configuration weights was done to include important configurations in the list of basic reference configurations used to construct a final set of configurations. These calculations are done by allowing single and double excitations to a much smaller 12*g* basis set, since the size of the computational problem will become prohibitive when additional reference configurations are included. The total contributions to including these extra configurations are given in the column “Extras” in Tab. 4. Beyond the initial 2 even- and 3 odd-parity configurations, we systematically included an additional 12 even- and 9 odd-parity reference configurations. Note that energies were calculated only for 2 even-parity levels to save computational resources and allow additional reference configurations. The inclusion of these extra configurations contributes about 100 cm⁻¹ shift to the energies and accounts for an additional 2 million configurations. Note also that these contributions would also be higher if the calculations were done with a larger basis set. We estimate an uncertainty from the convergence of the CI configuration set at the level of 50 cm⁻¹, which is essentially negligible in comparison with the basis set convergence uncertainty. We note that missing contributions can be both positive and negative in this case.

Analysis of contributions to the 3F-3G, 3C-3D, and 3A-3B line differences given in main text Table 3 shows that the basis set expansion contribution effectively cancels for similar configurations; it is less than 50 cm⁻¹ for all three cases. We also find that QED contributions play a major role in the 3F-3G energy difference. For 3C-3D, the contributions from the basis set expansion and addition of extra configurations essentially cancel out the QED. In the 3A-3B difference, the basis set and extra configuration contributions cancel, leaving a shift from the QED. Therefore, comparing the differences of the energy values for similar configurations provides important additional information. It would be very useful to improve the uncertainty of the experiment as well as carry out such comparison in other ions with different degrees of ionization with 7-10 electrons.

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