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Extended spectroscopic study of Ti XII with estimated QED contributions to the ground-state energy

M. Westerlind
Department of Physics, University of Lund, S-223 62 Lund, Sweden

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This paper presents an extended spectroscopic analysis of Na-like titanium, Ti XII, based on spectra recorded using the beam-foil method. About 30 new lines have been classified that have established ten new terms with high n and l quantum numbers. The new terms and combinations improve the established energy levels and allow for an accurate determination of the ionization limit from Ritz and polarization formulas. By comparison with a very elaborate relativistic calculation, the QED contribution to the ionization potential is estimated to be 849±20 cm^{-1}. An isoelectronic study of the ionization limit along the Na sequence is also presented.

I. INTRODUCTION

The spectra and term systems of Na-like ions have been extensively studied over the years. This interest originates in the simple electronic structure of these ions, i.e., one valence electron orbiting a closed-shell core. From a theoretical point of view, the relatively uncomplicated structure makes the Na-like ions suitable for testing different approximations, particularly for heavier elements where QED and relativistic effects are important. Experimentally there has been a renewed interest in Na-like ions because they have turned out to be a powerful tool in diagnosing fusion plasmas since the spectral lines are rather strong and easy to identify.

In 1988 Johnson, Blundell, and Sapirstein[1] published an extensive, relativistic calculation of the ionization potential, i.e., the binding energy of the 3s electron, for a number of ions along the isoelectronic sequence. This elaborate calculation, using the many-body perturbation method, includes virtually all energy effects except the QED contribution. Thus the latter can be obtained as the difference between the theoretical and experimental value of the ionization potential. This possibility stimulated the present effort to extend and improve the knowledge of the Ti XII term system with particular emphasis on obtaining an accurate ionization limit.

The spectrum of Ti XII has previously been investigated by Edlén,[2] Fawcett and Peacock,[3] Feldman and Cohen,[4] Ekberg and Svensson,[5] and Cohen and Behring.[6] Most of the work done in Ti XII and other heavy elements in the Na sequence has mainly dealt with the short-wavelength transitions to the $n=3$ shell, using different kinds of spark discharges and laser-produced plasmas as light sources. In the present work we have recorded new spectra of highly ionized titanium in the wavelength regions 335–1165 Å and 1300–1400 Å using the beam-foil technique. Combined with the earlier work, the term system has been extended to include all configurations up to 8k, except 8s. In addition, the levels 9p–11p and 9d–10d are known from the work by Cohen and Behring.[6]

The ionization limit was derived by fitting Ritz formulas to the np, nd, and nf series and by fitting polarization formulas to the nonpenetrating nf, ng, and nh series. The adopted value of 2 351 060±20 cm^{-1} is, within the quoted error, the same as in Ref. 5, but the uncertainty has been reduced by a factor of 3.

II. EXPERIMENTS

The Ti spectra were recorded at the 3-MV Pelletron tandem accelerator at the University of Lund. The ions were accelerated to an energy of 10 MeV and excited by the passage of a thin carbon foil. The emitted light was dispersed by a Minuteman 310 NIV 1-m normal-incidence vacuum monochromator equipped with a 2400 lines/mm grating blazed at 800 Å, and finally detected by a channeltron detector. The spectra cover the region 335–1165 and 1300–1400 Å. The latter region was recorded to obtain some $n=7$ to 8 transitions, and is shown in Fig. 1. The dominating spectra at 10 MeV are

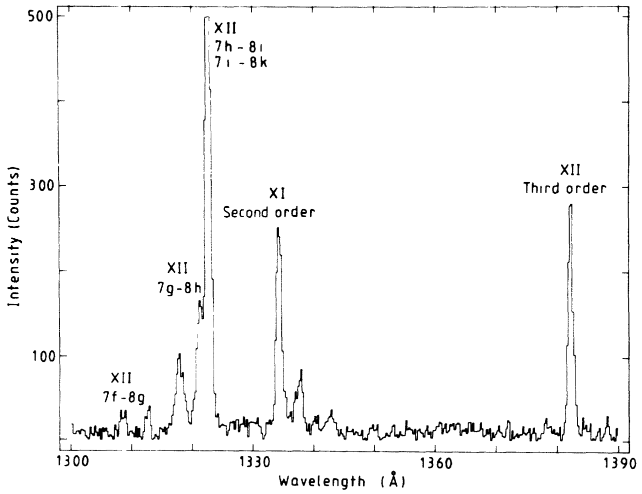

FIG. 1. Part of a beam-foil spectrum of Ti recorded at 10 MeV.

Mg-, Al-, and Si-like, but the spectrum of Ti XII is also very prominent. In the analysis we have also used beam-foil spectra recorded at 22 and 24 MeV at the 4-MV Dynamitron accelerator at Ruhr Universität Bochum, Federal Republic of Germany. These measurements were performed with a 2.2-m grazing-incidence monochromator with a 600 lines/mm grating and cover approximately the region 100–550 Å. A full description of these experiments is given in Ref. 7.

III. ANALYSIS

A. Wavelengths and term system

The wavelengths from the beam-foil recordings were obtained via a three-step procedure. First, peak positions were determined by running a program that determines the first and second derivatives of the observed intensities. In the second step, blended or unresolved structures were deconvoluted into Gaussian line shapes using the computer program CARATE.[8] Finally, the absolute wavelengths were determined by fitting a polynomial to known Ti lines in the foil-excited spectrum. In the 335–1165-Å spectrum a total of 40 uniformly distributed reference lines were used. With a third-degree polynomial, the average weighted deviation of the fit was 0.01 Å. The recordings made at higher energies and other wavelength regions were reanalyzed following the same procedure.

Table I contains all identified transitions in Ti XII including the lines from Refs. 5 and 6 since these have been utilized in our analysis. The wavelengths from Refs. 5

TABLE I. Observed transitions in Ti XII.

λ (Å)	λ_{obs}-λ_{calc} (Å)[a]	Transition
45.167[b]		$3s\,^2S_{1/2}-11p\,^2P$
45.783[b]		$3s\,^2S_{1/2}-10p\,^2P$
46.641[b]		$3s\,^2S_{1/2}-9p\,^2P$
47.906[b]		$3s\,^2S_{1/2}-8p\,^2P$
49.912[b]		$3s\,^2S_{1/2}-7p\,^2P$
50.448[b]		$3p\,^2P_{1/2}-10d\,^2D_{3/2}$
50.674[b]		$3p\,^2P_{3/2}-10d\,^2D_{5/2}$
51.446[b]		$3p\,^2P_{1/2}-9d\,^2D_{3/2}$
51.669[b]		$3p\,^2P_{3/2}-9d\,^2D_{5/2}$
52.896[c]		$3p\,^2P_{1/2}-8d\,^2D_{3/2}$
53.140[c]		$3p\,^2P_{3/2}-8d\,^2D_{5/2}$
53.433[c]	−0.002	$3s\,^2S_{1/2}-6p\,^2P_{3/2}$
53.457[c]	−0.003	$3s\,^2S_{1/2}-6p\,^2P_{1/2}$
55.181[c]	0.001	$3p\,^2P_{1/2}-7d\,^2D_{3/2}$
55.443[c]	0.000	$3p\,^2P_{3/2}-7d\,^2D_{5/2}$
56.161[c]	0.002	$3p\,^2P_{1/2}-7s\,^2S_{1/2}$
56.431[c]	−0.000	$3p\,^2P_{3/2}-7s\,^2S_{1/2}$
59.133[c]	0.001	$3p\,^2P_{1/2}-6d\,^2D_{3/2}$
59.435[c]	−0.001	$3p\,^2P_{3/2}-6d\,^2D_{5/2}$
60.701[c]	0.001	$3s\,^2S_{1/2}-5p\,^2P_{3/2}$
60.762[c]	−0.001	$3s\,^2S_{1/2}-5p\,^2P_{1/2}$
60.971[c]	0.006	$3p\,^2P_{1/2}-6s\,^2S_{1/2}$
61.286[c]	−0.003	$3p\,^2P_{3/2}-6s\,^2S_{1/2}$
62.433[c]	0.001	$3d\,^2D_{3/2}-8f\,^2F_{5/2}$
62.470[c]	0.003	$3d\,^2D_{5/2}-8f\,^2F_{7/2}$
65.540[c]	−0.002	$3d\,^2D_{3/2}-7f\,^2F_{5/2}$
65.577[c]	−0.002	$3d\,^2D_{5/2}-7f\,^2F_{7/2}$
67.171[c]	−0.001	$3p\,^2P_{1/2}-5d\,^2D_{3/2}$
67.555[c]	0.007	$3p\,^2P_{3/2}-5d\,^2D_{5/2}$
70.986[c]	−0.001	$3d\,^2D_{3/2}-6f\,^2F_{5/2}$
71.031[c]	0.001	$3d\,^2D_{5/2}-6f\,^2F_{7/2}$
71.545[c]	0.002	$3p\,^2P_{1/2}-5s\,^2S_{1/2}$
71.987[c]	−0.002	$3p\,^2P_{3/2}-5s\,^2S_{1/2}$
82.121[c]	−0.001	$3s\,^2S_{1/2}-4p\,^2P_{3/2}$
82.307[c]	−0.004	$3d\,^2D_{3/2}-5f\,^2F_{5/2}$
82.344[c]	−0.002	$3s\,^2S_{1/2}-4p\,^2P_{1/2}$
82.368[c]	−0.001	$3d\,^2D_{5/2}-5f\,^2F_{7/2}$
87.364[c]	−0.001	$3d\,^2D_{5/2}-5p\,^2P_{3/2}$
87.426[c]	−0.001	$3d\,^2D_{3/2}-5p\,^2P_{1/2}$
89.844[c]	−0.002	$3p\,^2P_{1/2}-4d\,^2D_{3/2}$
90.512[c]	0.000	$3p\,^2P_{3/2}-4d\,^2D_{5/2}$
108.086[c]	0.000	$3p\,^2P_{1/2}-4s\,^2S_{1/2}$
109.107[c]	0.000	$3p\,^2P_{3/2}-4s\,^2S_{1/2}$
116.497[c]	−0.002	$3d\,^2D_{3/2}-4f\,^2F_{5/2}$
116.597[c]	−0.001	$3d\,^2D_{5/2}-4f\,^2F_{7/2}$
127.84	−0.04	$4d\,^2D-8f\,^2F$
139.884[c]	0.001	$3d\,^2D_{5/2}-4p\,^2P_{3/2}$
140.361[c]	0.003	$3d\,^2D_{3/2}-4p\,^2P_{1/2}$
169.81	0.02	$4d\,^2D-6f\,^2F$
181.28	−0.04	$4f\,^2F-6g\,^2G$
208.45	0.02	$4p\,^2P_{3/2}-5d\,^2D_{5/2}$
253.07	0.00	$4d\,^2D-5f\,^2F$
258.24	0.02	$5f\,^2F-8g\,^2G$
279.03	0.00	$4f\,^2F-5g\,^2G$
320.94	−0.05	$5f\,^2F-7g\,^2G$
340.672[c]	0.000	$3p\,^2P_{1/2}-3d\,^2D_{3/2}$
349.929[c]	0.000	$3p\,^2P_{3/2}-3d\,^2D_{5/2}$
351.024[c]	0.000	$3p\,^2P_{3/2}-3d\,^2D_{3/2}$
460.741[c]	−0.004	$3s\,^2S_{1/2}-3p\,^2P_{3/2}$
468.78	−0.00	$5d\,^2D-6f\,^2F$
479.881[c]	0.005	$3s\,^2S_{1/2}-3p\,^2P_{1/2}$
492.80	−0.01	$5p\,^2P_{1/2}-6s\,^2S_{1/2}$
496.97	0.00	$5p\,^2P_{3/2}-6s\,^2S_{1/2}$
512.64	0.00	$5f\,^2F-6g\,^2G$
517.26		$5g\,^2G-6h\,^2H$
573.62	−0.01	$5d\,^2D_{3/2}-6p\,^2P_{3/2}$
574.85	0.00	$5d\,^2D_{5/2}-6p\,^2P_{3/2}$
576.50	0.01	$5d\,^2D_{3/2}-6p\,^2P_{1/2}$
670.13	0.01	$6p\,^2P_{3/2}-7d\,^2D$
780.37	0.00	$6d\,^2D-7f\,^2F$
849.54	0.01	$6f\,^2F-7g\,^2G$
857.55		$6g\,^2G-7h\,^2H$
858.43		$6h\,^2H-7i\,^2I$
934.50	0.00	$4p\,^2P_{1/2}-4d\,^2D_{3/2}$
959.945[c]	0.000	$4p\,^2P_{3/2}-4d\,^2D_{5/2}$
961.41	0.00	$6d\,^2D-7p\,^2P$
964.35	0.00	$4p\,^2P_{3/2}-4d\,^2D_{3/2}$
1308.42	0.00	$7f\,^2F-8g\,^2G$
1321.08		$7g\,^2G-8h\,^2H$
1322.58		$7h\,^2H-8i\,^2I$
1322.58		$7i\,^2I-8k\,^2K$

[a] Difference between observed wavelength and wavelength calculated from the least-squares fit of energy levels. This value is omitted when only one transition has been used to derive the upper level.

[b] Wavelength and classification from Ref. 6.

[c] Wavelength and classification from Ref. 5.

and 6 have an uncertainty of about 0.004 Å, whereas the beam-foil material has an accuracy of 0.04 Å. The 7 to 8 transitions, which occur above 1300 Å, have a uncertainty of 0.1 Å since no first spectral-order references could be used. The quoted wavelength uncertainty in the beam-foil material is determined by the reproducibility between different spectral orders and recordings made at different energies.

From the beam-foil recordings it has not been possible to resolve the fine-structure components in transitions from levels with $l \geq 3$, this is also true for transitions from *np* levels with $n \geq 7$. Most of the lines in the region 150–400 Å have been observed in the second and sometimes in the third spectral order, thus providing good opportunities to accurately determine wavelengths and check for possible blends. The number of observed blends is very small and fortunately mostly caused by transitions belonging to lower charge states, i.e., lines blended in the 10-MeV spectrum are found unblended in the high-energy spectra. The only two remaining blends are the $4p\,^2P_{3/2}$–$4d\,^2D_{5/2}$ at 959.8 Å blended by the strong resonance transition $3s\,^2S_{1/2}$–$3p\,^2P_{1/2}$ (479.9 Å) in the second order and the complete coincidence between $7h-8i$ and $7i-8k$ at 1323 Å; see Fig. 1.

In Table II we give the level energies, as derived from a least-squares fit of the wavelengths in Table I. The term system is also presented in Fig. 2, with some of the transitions indicated. Prior to this work no levels with $l > 3$ were known. We have now established the $5g-8g$, $6h-8h$, $7i-8i$, and $8k$ levels, as well as new combinations between the previously known levels. It is important to note that the new, long-wavelength lines observed in this work substantially improve the relative energies within the term system. This is due to the relation between wavelength and wave-number uncertainties, $\Delta\sigma = \Delta\lambda/\lambda^2$, which, for example, implies that a line at 80 Å with an accuracy of 0.004 Å has a wave-number uncertainty of 63 cm^{-1} while a transition at 800 Å measured to within 0.05 Å has a corresponding uncertainty of only 8 cm^{-1}. The relative level uncertainty in this work increases from about 5 to 160 cm^{-1} for the highest *np* and *nd* configurations, which are based on the short-wavelength transitions to 3*s* and 3*p* only.

TABLE II. Energy levels in Ti XII.

Level	E (cm^{-1})	ΔE[a]	Level	E (cm^{-1})	ΔE[a]
$3s\,^2S_{1/2}$	0		$5d\,^2D_{3/2}$	1 697 111	15
$4s\,^2S_{1/2}$	1 133 576	30	$5d\,^2D_{5/2}$	1 697 480	15
$5s\,^2S_{1/2}$	1 606 147	75	$6d\,^2D$	1 899 530	10
$6s\,^2S_{1/2}$	1 848 661	25	$7d\,^2D$	2 020 665	10
$7s\,^2S_{1/2}$	1 989 051	125	$8d\,^2D$	2 098 874	130
$3p\,^2P_{1/2}$	208 387	5	$9d\,^2D$	2 152 326	160
$3p\,^2P_{3/2}$	217 043	5	$10d\,^2D$	2 190 514	160
$4p\,^2P_{1/2}$	1 214 388	5	$4f\,^2F$	1 360 393	25
$4p\,^2P_{3/2}$	1 217 700	5	$5f\,^2F$	1 716 832	15
$5p\,^2P_{1/2}$	1 645 741	30	$6f\,^2F$	1 910 653	10
$5p\,^2P_{3/2}$	1 647 441	30	$7f\,^2F$	2 027 675	10
$6p\,^2P_{1/2}$	1 870 573	15	$8f\,^2F$	2 103 657	100
$6p\,^2P_{3/2}$	1 871 440	15	$5g\,^2G$	1 718 773	15
$7p\,^2P$	2 003 545	10	$6g\,^2G$	1 911 901	10
$8p\,^2P$	2 087 421	10	$7g\,^2G$	2 028 362	10
$9p\,^2P$	2 144 036	160	$8g\,^2G$	2 104 103	15
$10p\,^2P$	2 184 217	160	$6h\,^2H$	1 912 097	10
$11p\,^2P$	2 214 006	160	$7h\,^2H$	2 028 512	10
$3d\,^2D_{3/2}$	501 924	5	$8h\,^2H$	2 104 061	15
$3d\,^2D_{5/2}$	502 816	5	$7i\,^2I$	2 028 591	10
$4d\,^2D_{3/2}$	1 321 397	5	$8i\,^2I$	2 104 122	15
$4d\,^2D_{5/2}$	1 321 872	5	$8k\,^2K$	2 104 201	15
E_{limit} 2 351 060±20 cm^{-1}					

[a] Relative uncertainty, derived from the wave-number uncertainty and the number of combinations with a given level.

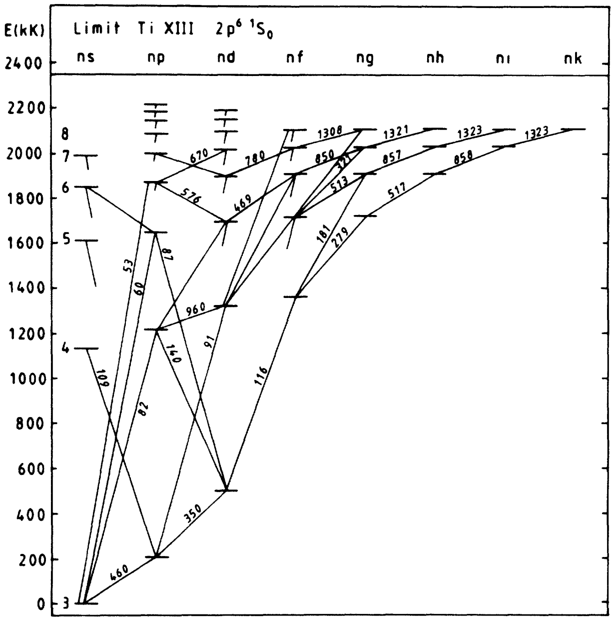

FIG. 2. Term diagram of Ti XII. Some of the observed transitions are indicated by their wavelength in Å.

Since it was not possible to resolve the fine-structure components in transitions from levels with $1 \geq 3$, a special procedure had to be used to obtain the best possible energy levels. Lines connecting the *nf* series with the 3*d* configuration were taken from Ref. 5 and had resolved fine structure. Assuming a hydrogenic splitting in the *nf* terms, we calculated $3d\,^2D_J-nf\,^2F_{\text{c.g.}}$ transitions and used these to establish the *nf* energy levels. As pointed out in Refs. 5 and 6, the calculated hydrogenic fine-structure splittings in the *nf* series are more accurate than those obtained directly from observations since the experimental wave-number uncertainty is larger than the splittings themselves. Lines from *nf* levels to $4d-6d$ were observed only as center-of-gravity transitions. In this case these lines were split into two components using the experimental fine structure in the *nd* series, as obtained from the $np-n'd$ transitions.

B. Ionization limit

The center-of-gravity energies of the *np*, *nd* and *nf* levels were used to fit Ritz formulas treating the ionization limit as an adjustable parameter. Three parameter formulas were fitted to the penetrating *np* and *nd* series while two parameters were sufficient for the *nf* terms. For the *nd* and *nf* series we obtained stable fits with an ionization potential in the range 2 351 060–2 351 080 cm^{-1} depending on the number of levels included in the fit. However, the *np* series seems to be less accurately described in this formalism. This problem has previously been noted and discussed by Cohen and Behring.[6] An inclusion of the highest *np* and *nd* levels ($n > 7$) gave slightly less accurate Ritz formulas; this could partly be due to Stark shifts of these levels.

For the hydrogenic, nonpenetrating, *nf*, *ng*, and *nh* terms we also applied the core-polarization formulation[9] to derive the ionization energy. In this formulation only two coefficients α_d and α_q are needed to describe the hydrogenic part of the term system. The two parameters are the dipole and quadrupole polarizabilities of the $2p^6$ core in units of a_0^3 and a_0^5 (where a_0 is the Bohr radius), respectively. Again treating the ionization limit as a parameter, its value is fitted simultaneously with α_d and α_q. The value of the ionization limit is rather insensitive to the number of levels included in the fit, e.g., using the *nf*, *ng*, and *nh* series gives 2 351 050 cm^1 for the limit, while exclusion of the whole *nh* series results in 2 351 048 cm^{-1}; a further exclusion of the 4*f* level affects the value by less than 10 cm^{-1}. However, the values of the α_d and α_q parameters are very sensitive to the number of levels included in the fit and the values adopted are those obtained when using the *nf*, *ng*, and *nh* series. In Fig. 3 we give an example of a polarization plot, as described by Edlén.[9] In the plot the 8*f* level appears to be a bit off the fitted line, but the deviation is within the wavelength uncertainty and excluding this point only affects the value of the ionization limit by about 2 cm^{-1}.

The agreement between the Ritz and polarization procedures and different series is good, and the adopted value of the ionization limit is 2 351 060±20 cm^{-1}. Within the quoted uncertainty this is the same as Ekberg and Svensson's value of 2 351 100±100 cm^{-1},[5] but with the error bars reduced by a factor of 3. The result also agrees with Edlén's semiempirical value of 2 351 074 cm^{-1}.[10] The resulting values of the parameters α_d and α_q are $(7.8\pm2.8)\times10^{-3}$ and $(8.6\pm1.0)\times10^{-3}$, respectively. Again this is in good agreement with Edlén's semiempirical predictions[10] of 10.4×10^{-3} and 7.86×10^{-3}. The polarizabilities have also been calculated by Johnson, Kolb, and Huang,[11] employing the relativistic random-phase approximation (RRPA), their value for α_d is 12.89×10^{-3} and for α_q, 2.159×10^{-3}. The agreement with our experimental value for α_d is quite good, while both our and Edlén's result for α_q are approximately a factor of 4 larger than the *ab initio* value. This situation is commonly observed in many isoelectronic sequences since the experimental value of the parameter α_q contains contributions from remaining penetration effects and higher multipole polarizabilities.

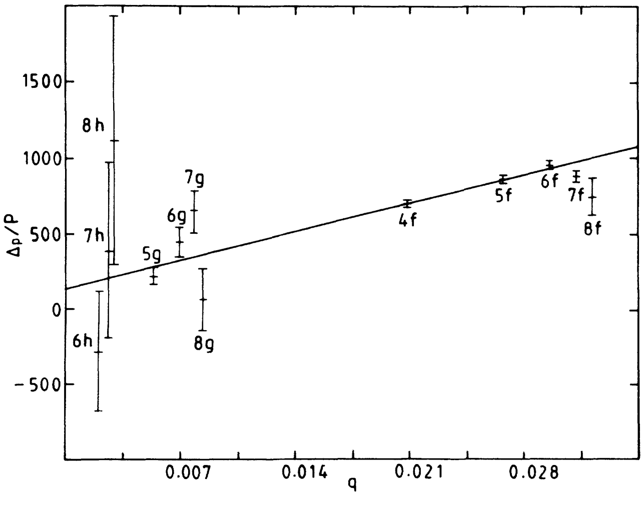

FIG. 3. Graphic illustration of the polarization formula, as described by Edlén in Ref. 9.

IV. IONIZATION LIMITS ALONG THE Na SEQUENCE

In Edlén's isoelectronic study of the Na sequence[10] the core-polarization formulation was applied to obtain accurate semiempirical values of the ionization limit along the sequence. However, several new results have appeared since the publication of this review. Thus Theodosiou and Curtis[12] have extended Edlén's work to include all

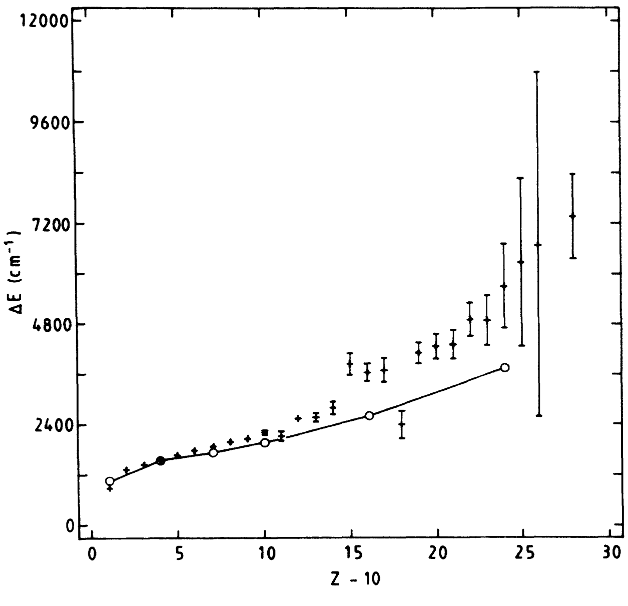

FIG. 4. The points with error bars are the differences between our nonrelativistic calculation and experimental values for the ionization limit in the Na sequence. The circles connected by straight lines are the differences between our calculation and the accurate, relativistic calculation by Johnson, Blundell, and Sapirstein (Ref. 1); see discussion in text. Experimental data: Na I (Ref. 14); Mg II (Ref. 15); Al III (Ref. 16); Si IV (Ref. 17); P V (Ref. 18); S VI (Ref. 19); Cl VII (Ref. 20); Ar VIII (Ref. 21); K IX and Ca X (Ref. 22); Sc XI (Ref. 5); Ti XII (this work); V XIII, Cr XIV, and Mn XV (Ref. 6); Fe XVI, Co XVII, and Ni XVIII (Ref. 23); Cu XIX, Zn XX, Ga XXI, Ge XXII, and As XXIII (Ref. 24); Se XXIV (Ref. 25); Br XXV (Ref. 26); Kr XXVI (Ref. 27); and Sr XXVIII (Ref. 28).

ions in the range $Z=30-54$, and also made isoelectronic extrapolations for some ions up to $Z=92$. In the present work we have studied the purely experimental values for the limits without any attempts to improve the values besides Ti XII. To make an isoelectronic comparison of the ionization limits in the Na-isoelectronic sequence we have performed simple, nonrelativistic calculations of the limits using the Cowan code.[13] Figure 4 shows a plot of the differences between calculated and experimental values (with error bars from the experimental uncertainties). From the figure it is obvious that the Ni XVIII point is off the isoelectronic trend and hence should be remeasured. The experimental values for Sc XI, V XIII, Cr XIV, and Mn XV are taken from the work by Cohen and Behring[6] and are derived from Ritz formulas. However, they also give an alternative set of data, based on the polarization formulation, which is in slightly better agreement with the isoelectronic trend but, since these are obtained by using semiempirical values of α_d and α_q, we have chosen to use their purely experimental results for the ionization limits.

The theoretical results of Johnson, Blundell, and Sapirstein[1] are also included in Fig. 4. For low Z we note that theory and experiment are quite close, while they differ by a few thousand cm^{-1} for high Z, where the QED effects become large. An interpolation of the theoretical data gives the value 2 351 909 cm^{-1} for the ionization limit in Ti XII, which is 849 cm^{-1} larger than our experimental value. Thus the QED contribution to the limit is estimated to 849 ± 20 cm^{-1}, i.e., with a relative error of 2% only. By comparison, the relative errors in ions close to Ti XII are 15% in Ca X and 20% in Fe XVI. For other ions, where Johnson, Blundell, and Sapirstein have made calculations, the relative error increases from about 5% for the lower ionization stages up roughly 50% for the highest-Z elements. Thus analyses like the present investigation of Ti, where longer-wavelength transitions are used to improve the relative energy levels and hence the accuracy of the ionization limit, would be desirable for higher-Z elements where the QED contributions become even more important.

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