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Measurement of long-range interaction effects for Rydberg state transitions in berylliumlike ions

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A spectroscopic measurement of the $1s^2 2s7I$-$1s^2 2s8K$ Rydberg transition energy in berylliumlike S XIII is presented as a high-Z test of long-range electron-ion interactions. The observed deviation from the Dirac energy (7×10^{-4}) is compared with atomic core-polarization models and with relativistic atomic structure calculations.

High-angular-momentum Rydberg states in berylliumlike ions represent the simplest atomic states in which large deviations from hydrogenlike energies are expected to be dominated by long-range electron-ion interactions. Sufficiently high principal (n) and orbital (l) quantum number states should be free of significant penetration effects that involve overlap of the Rydberg electron with the lithiumlike ($1s^2 2s$) atomic core. Also, these high-angular-momentum (high-L) states do not experience strong perturbation effects that could arise from interaction with nearby excited states. The unperturbed high-L Rydberg energies may then be described by a nonpenetrating electron-ion interaction that is expressible in terms of multipole polarizabilities of the alkali-metal-like atomic core.[1-4] Such modeling of polarization corrections in simpler alkali-metal-like ions with weakly polarizable inert-gas-like cores has proven to be successful in representing spectroscopically observed transition energies involving moderately high-angular-momentum states.[2,5] In berylliumlike ions, the lithiumlike core with its single L-shell electron contributes large polarizability corrections to Rydberg levels, allowing much greater spectroscopic sensitivity to polarization structures. Measurements for low-Z berylliumlike ions ($Z \leq 9$) have shown that parametrized core-polarizability models partially based upon the long-range electron-ion interaction are capable of predicting certain Rydberg transition energies in these systems.[6,7] There is a clear need for studies of berylliumlike Rydberg spectra in higher-Z ions in order to clarify the validity of polarization models by expanding the charge state range over which the significance of specific Z-dependent contributions can be tested.[3,4] We emphasize that spectroscopic measurements of Rydberg transitions provide the only available experimental method for determining core polarizabilities in highly-ionized atoms. Furthermore, only a low-density field-free source such as the fast-ion (beam-foil) excitation method is able to produce undistorted spectra for high-L states in highly-ionized atoms.

Beyond the unique association with atomic core polarizabilities, the accurate spectroscopic description of high-angular-momentum states in high-Z berylliumlike ions will lead naturally to a better initial understanding of the energies of perturbed lower-L Rydberg states.[8] With increased knowledge of these structures, the prominent appearance of such high-Z Rydberg transitions in fast-ion-beam sources is potentially applicable to the formulation of high-n excited-state population mechanisms, to the determination of reliable ionization energies in high charge states, and to the establishment of in-beam reference wavelength values for highly-ionized atoms. Moreover, the recent observation of high-Z berylliumlike Rydberg transitions in a low-density high-temperature plasma appears to be promising as a potential plasma diagnostic involving highly-ionized atoms.[9,10]

For this Rapid Communication, we have chosen the $1s^2 2s7I$-$1s^2 2s8K$ transition in S XIII ($Z=16$) as a measurable Rydberg state transition in a high-Z berylliumlike ion that is particularly suitable for comparison with polarization models and with relativistic calculations. Only this highest-angular-momentum component, $L=6$-7, of the $n=7$-8 transition is expected to be free of strong perturbations that arise from configuration mixing, since there are no nearby perturbing states ($1s^2 2pnl$) with the same total angular momentum and parity. The angular momentum also appears to be sufficiently high to avoid appreciable core penetration effects. In addition, the $7I$-$8K$ transition in isoelectronic Cl XIV has previously been the subject of theoretical study in one polarization model formulation.[3] We have observed the spectrum of the $n=7$-8 transition structure in S XIII, and we report here our measured wavelength (transition energy) for the highest angular momentum $7I$-$8K$ component. This work represents the measurement of resolved high-angular-momentum structure in a high-Z berylliumlike Rydberg transition that is sensitive to the effects of long-range electron-ion interactions. We compare our measured value for the $7I$-$8K$ transition energy with polarization model formulations as well as with relativistic atomic structure calculations. In particular, these measurements provide a test of relativistic many-body perturbation theory calculations for high-angular-momentum states in berylliumlike ions.[11]

The spectrum of S XIII was produced by ionization and excitation of a beam of 58-MeV sulfur ions directed through a carbon-foil target of areal density 30 μg/cm^2, which promoted about 30% of the ions to the berylliumlike S^{12+} charge state. The fluorescent spectrum from the excited sulfur beam was observed using a 1-m normal incidence vacuum ultraviolet monochromator and a channeltron photon-counting detector. The spectrum was scanned in wavelength by means of a computer-controlled stepping-motor-driven precision translation and rotation mechanism for the monochromator grating.

A single wavelength scan of the spectrum of foil-excited highly-ionized sulfur near the berylliumlike $n=7$–8 transition is shown in Fig. 1. The instrumentally determined wavelength resolution is about 1 Å. The strong line observed near 1126 Å is expected to be dominated by the highest-L components of the S XIII $n=7$–8 Rydberg transition, as is characteristic of the angular momentum structure produced by the ion-foil excitation mechanism.[12] We have performed multiconfiguration Dirac-Fock (MCDF) calculations of this transition structure using the Grant[13] and GRASP codes.[14] These calculations confirm that the $7I$-$8K$ highest-angular-momentum component is concentrated in the strongest peak, with part of the $7H$-$8I$ second highest-angular-momentum component producing the peak near 1131 Å. All the remaining lower-angular-momentum structures of the $n=7$-8 transition are strongly perturbed and are predicted to lie outside the region shown in the figure. These structures, as well as the weak features between 1110–1125 Å, will be discussed in detail elsewhere. Also observed in the spectrum are three unperturbed Rydberg transitions from heliumlike and lithiumlike sulfur: $n=6$–7 in S XV (in second order) at 1098.84 Å, $n=9$–11 in S XIV at 1139.15 Å, and $n=5$–6 in S XIV (in third order) at 1140.81 Å. These wavelengths are accurately calculable as unresolved polarization-corrected hydrogenlike values,[15,16] and they provide the Doppler-corrected wavelength scale for this measured spectrum.

The S XIII $7I$-$8K$ transition and the three S XIV and S XV Rydberg transitions were fit to Gaussian line profiles. A Doppler-corrected wavelength dispersion for the spectrum was determined using the three Rydberg lines as reference wavelengths, which then yielded the fitted wavelength value for the $7I$-$8K$ transition of 1126.41 Å. The total uncertainty to be applied to this measured wavelength value is composed of several contributions of comparable magnitude. The statistics of the fitted profiles provide a combined uncertainty of ± 0.05 Å. Possible instrumental nonlinearities in the dispersion scale are estimated to contribute ± 0.05 Å. The influence of blended lines in the spectrum, such as those mentioned above, may contribute up to ± 0.08 Å. The spectrum fit for the wavelength dispersion produced an uncertainty of ± 0.11 Å, primarily due to uncertainties in the wavelength values of the references lines. These four contributions were summed in quadrature to yield a final value for the $7I$-$8K$ transition wavelength in S XIII of 1126.41 ± 0.15 Å, which corresponds to a transition energy (E/hc) of 88778 ± 12 cm^{-1}.

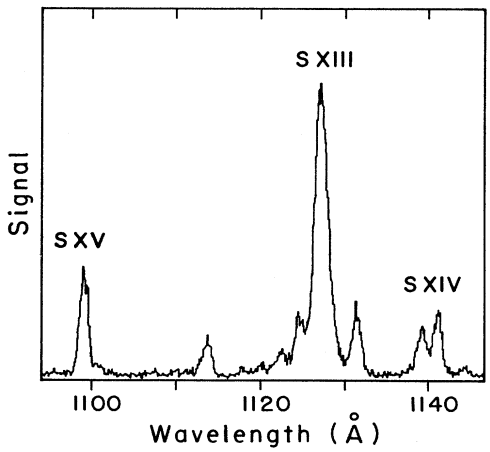

FIG. 1. Observed spectrum of high-L structure of the $n=7$–8 Rydberg transition in S XIII, and of three Rydberg transitions in S XIV and S XV.

The strongly hydrogenic character of high-angular-momentum Rydberg state transitions is apparent by comparison of our measured value for the $1s^2 2s\,7I$-$1s^2 2s\,8K$ transition wavelength in berylliumlike S XIII with the value for the $7I$-$8K$ transition in hydrogenlike Al XIII. The S XIII wavelength lies about 0.8 Å lower than the Dirac fine-structure values[17] for Al XIII of 1127.16 and 1127.24 Å. This blueshift amounting to 0.07% of the transition wavelength is ten times larger than the magnitude of the Dirac fine-structure wavelength interval, and reflects the effect of incomplete nuclear charge screening by the three $(1s^2 2s)$ core electrons in S XIII. We consider below three different methods of calculating this measured nonhydrogenic behavior for high-angular-momentum states in berylliumlike ions.

A simple modeling of the long-range electron-ion interaction for nonpenetrating high-angular-momentum states is provided by the core-polarization formulation, in which the inner electrons are treated as a deformable core of charge that adjusts the Rydberg state energy through parametrized core polarizability contributions.[2,6] The Rydberg state term energy (magnitude of the binding energy) is then customarily represented by

$$T = T_H + A\langle r^{-4}\rangle + B\langle r^{-6}\rangle ,$$

where T_H and $\langle r^{-x}\rangle$ are the spin-averaged term energy and radial expectation values for the corresponding hydrogenlike ion, and A and B are the atomic core parameters. Usually the associations $A=\alpha_d$ and $B=(\alpha_q - 6\beta)$ are adopted, where α_d and α_q are the dipole and quadrupole polarizabilities of the core and β is a nonadiabatic (or dynamical) correction. Thus the polarizability contributions reflect attractive interactions, whereas the dynamical correction is repulsive. Using the calculated values $\alpha_d = 0.0813 a_0^3$, $\alpha_q = 0.00169 a_0^5$, and $\beta = 0.0366 a_0^5$ from Ref. 6, which are based upon sums of oscillator strengths, and tabulations of $\langle r^{-x}\rangle$ from Ref. 2, the total $\langle r^{-4}\rangle$ correction for the $7I$-$8K$ transition wavelength in S XIII is -0.6 Å and the total $\langle r^{-6}\rangle$ correction is $+0.3$ Å. These values are consistent to within a few percent with the polarization corrections obtained by Z-dependent scaling of polarizability and dynamical term contributions calculated specifically for the $7I$-$8K$ transition in berylliumlike Cl XIV.[3] In the $\langle r^{-6}\rangle$ term for S XIII, the quadrupole polarizability contribution is less than 1%, so that the parameter B is essentially equal to the repulsive dynamical term (-6β). The resultant total $\langle r^{-4}\rangle$ and $\langle r^{-6}\rangle$ polarization correction to the hydrogenlike wavelength of -0.3 Å is not consistent with our measured shift of -0.80 ± 0.15 Å (see Table I). There are a number of possible reasons for this disagreement between measurement and the long-range interaction model. The discrepancy could simply arise from inaccurate polarizability and dynamical

TABLE I. Comparison of the measured wavelength (in Å) of the $1s^2 2s7I$-$1s^2 2s8K$ transition in SXIII with calculated values.

				MCDF [c]		
		Polarization model [b]				
J_{7I}-J_{8K}	Experiment [a]	$\langle r^{-4}\rangle$	$\langle r^{-4}\rangle+\langle r^{-6}\rangle$	Single configuration	Perturbed	MBPT [d]
5-6	1126.41 ± 0.15	1126.6	1126.9	1127.15	1126.33	1126.17
6-7(−)				1127.14	1126.41	
6-7(+)				1127.23	1126.40	
7-8				1127.21	1126.49	1126.32

[a]This work.
[b]Calculated from Curtis (Ref. 6) and Dalgarno and Shorer (Ref. 3) (extrapolated).
[c]Calculated using the Grant (Ref. 13) and GRASP (Ref. 14) codes.
[d]W. R. Johnson and J. Sapirstein (Ref. 11).

term values, although reasonable consistency among several calculations, especially for α_d, appears to preclude this possibility.[6] We note also that relativistic corrections to the dipole polarizability are expected to contribute only at the level of ~2%.[3] Alternatively, the assumption of negligible penetration corrections for the Rydberg electron[3] may not be correct in such a high-Z berylliumlike ion, even for these large values of angular momentum. More generally, the detailed form of the polarization model itself may be partially inappropriate for berylliumlike ions,[4] in particular with regard to the magnitude and sign of the dynamical term. Finally, the presence of very weak but significant configuration mixing contributions (see below) is not directly accounted for by the polarization model, and this may distort the interpretation that the measured nonhydrogenic behavior represents only the effects of long-range electron-ion interactions.

In order to provide comparison between a direct calculation of the berylliumlike transition wavelength and our measured value, we have performed detailed MCDF calculations of the $7I$-$8K$ fine-structure transition energies in SXIII. The absence of nearby perturbing states for either the $2s7I$ or $2s8K$ levels in SXIII suggests that a single-configuration calculation should yield a reasonably accurate value for the $7I$-$8K$ energy interval. We have calculated the single-configuration MCDF wavelength results for SXIII and found them to be nearly identical to the Dirac fine-structure wavelength values for hydrogenlike AlXIII (see Table I). The single-configuration results do not account for our measured shift of −0.8 Å and also do not reflect the expected size of polarization contributions. Therefore we have explored the effects of very weak configuration mixing in our MCDF calculations for these excited states. The energetically closest possible perturbing states for our high-angular-momentum levels are $1s^2 2p6h$ for the $2s7I$ level and $1s^2 2p7i$ for the $2s8K$ level. Both of these nearest perturbers lie more than 10 eV higher in energy than their respective perturbees, and would not be expected to strongly influence them. (Note that the total $2s7I$-$2s8K$ energy interval itself is only about 11 eV.) However, we have found the small influences of these distant perturbing states to be significant at our level of experimental sensitivity. The $2s7I$ fine-structure states are mixed at the level of ~0.08% with $2p6h$, perturbing the $2s7I$ states downward and producing a shift in the $7I$-$8K$ fine-structure wavelengths of approximately −1.0 Å. Inclusion of the still weaker (~0.01%) mixing of $2p7i$ with $2s8K$ perturbs the $2s8K$ fine-structure states downward as well and contributes about a +0.2 Å shift to the $7I$-$8K$ wavelengths. The resultant MCDF perturbed $(2s7I+2p6h)$-$(2s8K+2p7i)$ fine-structure wavelengths are in excellent agreement with our measured value for the unresolved transition wavelength (see Table I). All our attempts to include other (more distant) perturbing states yielded no significant additional shifts of the $7I$-$8K$ wavelengths.

A more sophisticated treatment of berylliumlike Rydberg state energies is provided by relativistic many-body perturbation theory (MBPT) calculations. In response to our measurements, this powerful technique has been very recently applied to the $7I$-$8K$ transition in SXIII.[11] For these high-angular-momentum states, inclusion of terms at least to second order in MBPT is needed to reflect significant departures from Dirac values, such as those represented by polarization contributions. The MBPT wavelength results to second order for two of the fine-structure components ($7I_{5,7}$-$8K_{6,8}$) in SXIII (Ref. 11) are shown in Table I. (The two spin-orbit mixed $J=6$-7 fine-structure components are not yet available from these calculations.) The MBPT results are in good agreement with our measured value, and differ from the corresponding MCDF fine structure values by less than 0.2 Å. This small (1.5×10^{-4}) discrepancy between the MCDF and MBPT transitions energies presumably reflects the complete accounting for electron correlation, including all possible perturbing states, that characterizes the MBPT calculations.

In conclusion, we have measured the transition energy for the highest-angular-momentum component of the $n=7$-8 Rydberg transition in berylliumlike SXIII to reveal a deviation from the Dirac value that reflects the effects of long-range electron-ion interactions expressed in terms of atomic core polarizabilities and nonadiabatic contributions. However, the polarization model corresponding to these long-range interactions does not account for the entire measured deviation, which may signify a deficiency in the model or the presence of additional physical contributions. Relativistic MBPT and MCDF calcu-

lations show good agreement with the measurement, which suggests that the effects of core polarization and weak configuration mixing in this transition energy are simultaneously accounted for to an accuracy of ~ 10 cm^{-1} (or $\sim 5\times 10^{-5}$ a.u.) both by the limited multiconfiguration basis used in the MCDF method and by the core excitations inherent in MBPT. The present measurement is the first study in berylliumlike ions for $Z > 9$ that has provided sensitivity to the core polarization effects without experiencing the overwhelming influence of strong configuration mixing. Additional spectroscopic measurements of Rydberg transition energies in high-Z berylliumlike ions, especially for nonpenetrating, unperturbed higher-L states, are needed to further quantify the suitability of spectroscopic core polarization contributions as a representation of long range electron-ion interactions in these simplest alkaline-earth systems.

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