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IDENTIFICATION OF RYDBERG STATES IN THE ATOMIC LANTHANIDES AND ACTINIDES*

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1. Introduction

An accurate determination of an atomic ionization potential usually requires an observation of a Rydberg progression or the determination of a photoionization threshold. In the lanthanides and the actinides direct measurements of limit values using conventional techniques are prohibitively difficult. For example, a uv absorption spectrum is usually hard to interpret due to the existence of many high (low) lying states of low (high) lying valence configurations. Transitions to these high lying valence states are stronger and more numerous than transitions to Rydberg states. As a rule, Rydberg series are hopelessly obscured in the absorption spectrum. Similarly, uv photoionization spectra are complicated by transitions from many low lying metastable levels that have significant populations at the temperatures at which the atomic species have reasonable vapor pressures. Usually, photoionization occurs at wavelengths significantly longer than that necessary to ionize ground state atoms. It is nearly an impossible task to separate the photoionization spectral originations on the atomic ground state from that on the metastable states. While long Rydberg series in 3 lanthanide elements have been identified using conventional methods [1,2], more sensitive and flexible methods are required to systematically study these heavy multi-electron atoms.

About one year ago we reported the detection of several Rydberg series in atomic uranium [3]. This was the first observation of Rydberg progressions in any actinide. In these experiments high lying states were accessed by time resolved stepwise excitation using pulsed dye lasers tuned to resonant transitions. Atoms excited to levels within 1000 cm⁻¹ of the ionization limit were then photoionized by 10.6 μ radiation from a pulsed CO₂ laser. By delaying the infrared ionizing pulse, and thus discriminating against short lived valence states, longer lived Rydberg states having $n > 14$ were observed. Series convergences yielded a very precise value for the uranium

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ionization limit (6.1941(5) eV or 49358(4) cm^{-1}). We would now like to report the study of Rydberg spectra and ionization thresholds of ten lanthanides using several variations of this time-resolved resonant multistep technique. The ionization limits for the lanthanides determined in this way show a systematic dependence on atomic number. We offer a simple physical model to explain these results.

2. Experimental Methods

The experimental apparatus is shown schematically in Fig. 1. Briefly, the apparatus is a crossed beam spectrometer in which the atomic beam is irradiated and eventually ionized by the output of two or three pulsed dye lasers tuned to resonant transitions. The oven consists of a resistively heated tungsten crucible operated at temperatures to give a vapor pressure of about 10^{-5} torr of the atomic species under study. The vapor issues through a slit into an interaction chamber where the number density is $10^9 - 10^{11}$ atoms/ cm^3 . The chamber is electrically biased to suppress thermal ions from the oven and to efficiently focus photoion product into the detection system. The detector is a channeltron particle multiplier contained within a quadrupole mass analyzer. The excitation sources are N_2 laser pumped dye lasers which provide 5-10 nsec pulses having 0.5-1.0 cm^{-1} spectral line widths. The separate N_2 lasers are fired by a common master trigger. The master control unit also provides a pulse to trigger the gate of a boxcar which in turn integrates the signal from the particle multiplier. Wavelength calibrations are provided by emission lines from either a uranium or thorium microwave electrodeless discharge lamp.

Figure 1. Laser spectroscopy apparatus.

The experimental procedure is to first identify a threshold for photoionization in the atom under study to an accuracy of ten to twenty wavenumbers using a two step photoionization process from several parent levels. Once this threshold value is well established, the photoionizing laser is next tuned through regions in the ionization spectrum where one would expect

to observe autoionizing Rydberg states which converge to well known low lying excited states of the ion. The two lasers are generally delayed in time by about 10 nanoseconds to provide an unambiguous excitation sequence. That is, the first laser is held at wavelength λ_1 to bring the atom to an excited state near 3 eV. The second laser, which is scanned in wavelength λ_2 , ionizes the atom when the combined energy of the two laser frequencies exceeds the ionization energy of the atom. If necessary, three step photoionization studies are also performed. As before, a small time delay between the output of the lasers is introduced to provide an unambiguous excitation sequence of λ_1 then λ_2 and finally λ_3 . A threshold for photoionization is determined to check the two laser two photon results. This is followed by a search for autoionizing Rydberg states. All experiments consist of monitoring the photoion production as a function of the continuously scanned final wavelength.

Figure 2 illustrates an autoionizing Rydberg series in Dy. We have also observed autoionizing progressions in Nd, Sm, Eu and Er. In some cases autoionizing series are obscured by the large density of non-Rydberg autoionizing states. This was the situation in our original work on U. In those cases we employed time resolved ionization techniques. The atom is brought to a state just below the ionization limit, and is subsequently ionized by a pulsed electric field[4] or by collisions with other atoms in the beam[5]. Bound Rydberg states are preferentially ionized and detected because they are long lived and highly polarizable. Figure 3 shows a bound Rydberg series in Ce converging to the ground state of the ion obtained using the time delayed (~2 μ sec) field ionization method. We have also observed bound Rydberg series in Gd and Tb in this way. Collisional ionization was used to detect bound Rydberg series in Ho, as illustrated in Fig. 4.

Figure 2. Dysprosium autoionizing Rydberg series converging to the $4f_{15/2}$ limit 820.3 cm^{-1} above the $4f_{17/2}$ ground state of the ion. This is a double series converging to the same limit.

Figure 3. Cerium series converging to the $4H_{7/2}$ ground state obtained by pulsed field ionization of the bound Rydberg levels. The pulsed field of 100 V/cm was delayed 4 μ s from the populating laser pulse.

Figure 4. Collisionally ionized Rydberg series of holmium converging to the $5I_8$ ground state of the ion. The excitation sequence is shown with collisional ionization indicated by the wavy arrow.

3. Results

We have observed Rydberg progressions in U, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho and Er. With the exception of Pr and Pm, series have been observed in all

the lanthanides since Rydberg spectra in Eu, Tm and Yb have been reported in the literature [1,2]. The criterion we used in determining an ionization limit is to choose that value which yields the smoothest and most constant value of the quantum defect as a function of n for the high Rydberg states. This procedure ignores the effects of perturbations in the spectrum which can cause sudden deviations in the quantum defect from state to state. For very high principal quantum number states, however, such deviations are unlikely to cause an error larger than a few wavenumbers. In those cases where the effects of perturbations are obviously present, that is when smooth progressions over an extended range are not observed, we have adopted larger error bars in our quoted values for the ionization limits. Figure 5 shows

Figure 5. Variation in quantum defect ($n - n^*$) vs n with change in assumed limit for the Cerium Rydberg series shown in Fig. 3.

the variations in quantum defect ($n - n^*$) for a change in the assumed limit value for a field ionized band series in Ce. The value of n is not necessarily the principal quantum number but is a running integer chosen close to n^* in order to evaluate the variation in quantum defect. The sensitive dependence of the slope of the quantum defect curve on the assumed ionization limit is quite evident, and illustrates the usefulness of this procedure in extracting a series convergence limit. For Pr, we derived a value for the ionization limit from the observed sharp onsets of photoionization.

Table 1 lists the lanthanide ionization limits that we have measured. The typical uncertainties are .0005 eV for Rydberg convergence and .005 eV for photoionization thresholds. The ionization limit listed for Pa was obtained using the interpolation procedure described in the next section. Our measured limit for Eu overlaps the earlier more accurate determination of Smith and Tomkins [2]. The values for Tm and Yb are taken from Camus [1]. The best previous values for the other lanthanides are those of Reader and Sugar [6] who used a spectroscopic extrapolation procedure. For several cases our direct measurements are outside of their .008-.050 eV error bars. The electron impact values of Ackermann et al. [7] have quoted uncertainties of 0.1 eV.

Table 1 LANTHANIDE FIRST IONIZATION POTENTIALS

<u>Element</u>	<u>Electron Impact Ref. 7</u>	<u>Spectroscopic Extrapolation Ref. 6</u>	<u>Laser Spectroscopy LLL</u>	
			<u>Photoionization Threshold</u>	<u>Rydberg Convergence</u>
Ce	5.44	5.47(5)	5.537(4)	5.5387(4)
Pr	5.37	5.42(3)	5.464(6)	---
Nd	5.49	5.489(20)	5.523(3)	5.5250(6)
Pm	---	5.554(20)	---	[5.582(10)]
Sm	5.58	5.631(20)	5.639(3)	5.6437(10)
Eu	5.68	5.67045(2) ^a	5.666(3)	5.6704(3)
Gd	6.24	6.141(20)	---	6.1502(6)
Tb	5.84	5.852(20)	---	5.8639(6)
Dy	5.90	5.927(8)	5.936(3)	5.9390(6)
Ho	5.99	6.018(20)	6.017(3)	6.0216(6)
Er	5.93	6.101(20)	6.104(3)	6.1077(6)
Tm	6.11	6.18436(20) ^b	---	---
Yb	6.21	6.25394(20) ^b	---	---

() = error in last digit

[] = extrapolated value

^aTaken from reference 2^bTaken from reference 1We have used the conversion $1 \text{ eV} = 8065.479 \text{ cm}^{-1}$.

Figure 6. Normalized ionization potentials of the lanthanides plotted as a function of number of f electrons. Only the Ce and Gd points required normalization to the $4f^N 6s^2 - 4f^N 6s$ process, see text.

4. Discussion

With the exception of Ce and Gd, the ionization process is a removal of an s electron from the $4f^N 6s^2$ ($N = 2$ to 14) configuration, and the ionization potential is the difference between the energy of the lowest level of the $4f^N 6s^2$ configuration of the neutral and the lowest level of the $4f^N 6s$ configuration of the ion. For Ce ($N = 2$) and Gd ($N = 8$) the ground configurations for the neutral are $4f^0 1d^0 6s^2$. The ground ionic configuration of Ce is $4f^1 1d^0$ and that for Gd is $4f^7 1d^0 6s$. However, the positions of the lowest lying levels of the $4f^N 6s^2$ and $4f^N 6s$ configurations are known very accurately from spectroscopic studies [7]. We can therefore normalize our results so that all the ionization limits correspond to the removal of an s electron from the lowest level of $4f^N 6s^2$. The resulting data is plotted in Fig. 6. The values for Tm and Yb are taken from reference 1. The ionization limits normalized in this way clearly show a piecewise linear variation with a change of slope at the half shell ($N = 7$). This behavior is not specific to the lanthanides as illustrated in Figs. 7 and 8 in which the normalized ionizations limits for the first short period ($2p^N 2s^2 - 2p^N 2s$) and the iron transition series ($3d^N 4s^2 - 3d^N 4s$) are plotted as a function of N . In all cases the limit corresponding to the difference in energy between the lowest levels of the $n^N n's^2$ configuration of the neutral and $n^N n's$ of the ion has the same characteristic piecewise linear dependence on N with a slope break at the half-shell. To our knowledge this is the first time that a systematic dependence of ionization limit on atomic number within a period has been clearly shown.

This behavior for the normalized limit values can be explained simply in terms of the Pauli exclusion principle and Hund's rule. Consider the ionization process $n^N n's^2 - n^N n's$. In the absence of correlation between the

Figure 7. Normalized ionization potentials for the 2p series. In each case a correction for the ion from $2s^2 2p^{N-1}$ to $2s2p^N$ was required to normalize the ionization process to $2s^2 2p^N - 2s2p^N$.

Figure 8. Normalized ionization potentials for the 3d series. Corrections were necessary for V, Cr, Co, Ni and Cu to normalize the ionization process to $3d^4 4s^2 - 3d^4 4s$.

electrons motions and positions the ionization energy we associate with this configuration change will increase uniformly with N because of incomplete electrostatic shielding. However, the exclusion principle constrains the electrons motions to be correlated through its requirement that the multi-electron wave function be anti-symmetrized. Hund's rule dictates that the state which has the highest spin multiplicity lies lowest in energy. As one proceeds to the half filled shell in the ion ($nd^n s$) the s electron has its spin aligned along the parallel spins of the $n f$ -orbital electrons. This reduces the electrostatic repulsion energy in the ground ionic state as a function of atomic number because the s electron is forced to spatially avoid in a pairwise way each of the $n f$ -orbital electrons. As a result this additional interaction will depress, monotonically with N , the ionization energy that would exist in the absence of exchange. In fact, this is the origin of Hund's rule. However, after the shell has been half filled, the f -orbital electrons start pairing and the exchange effect reverses. Every unit change in N lifts the constraints on electron overlap and thus reduces the lowering of the ionization energy. Paired s electrons make no contribution to this symmetry dependent energy; only the ion with its single s electron is affected by the spin alignment of the partially filled shell.

Under the assumption that the f - and s -orbitals do not change as the f shell is progressively filled, Slater-Condon theory [9] predicts this piecewise linear behavior with a break of slope at the half-shell. In fact, the slope change is identically the exchange integral $G_2(2s)$ of the ion. Fortunately, these conditions are approximately satisfied by the lanthanides. The least squares fit to our experimental data (solid line figure 6) yields a slope difference of $220(23) \text{ cm}^{-1}$ which is in excellent agreement with the average value of $G_2(2s) = 210(10)$ determined from the parameterized fitting of energy levels in the lanthanides [10]. This demonstrates that the exchange effect is indeed responsible for the slope break. Unfortunately, the Slater-Condon approach is not very useful in describing the behavior of the other series because in these cases the Slater parameters vary drastically across the periods.

Kathy Rajnak and Bruce Shore of our laboratory have extended the analysis by performing *ab initio* Hartree-Fock (HF) calculations [11]. In all cases (Figs. 6, 7 and 8), the HF results show the same piecewise linear behavior with a slope break at the half-shell. In fact, the HF calculations reproduce the slope difference for the first period and transition metal series, as well as the lanthanides, quite accurately. Although the HF calculations fail to predict the absolute ionization limits, they can be shifted to fit the experimental data because they have the correct dependence on N . In this way we hope to accurately predict the ionization potentials in the actinides based on our knowledge of the limit in U.

The Rydberg series we have reported were taken with a resolution ($0.5\text{--}1.0 \text{ cm}^{-1}$) sufficient to extract a good value of the ionization limit, but insufficient to study spectral perturbations. Thus the errors in our extrapolated ionization limits reflect in part the variations in the quantum defects. In order to understand the nature and the magnitude of perturbations on Rydberg states in very heavy multi-electron atoms we have initiated an experimental program to measure absolute level energies of Rydberg states in atomic uranium to 0.01 cm^{-1} precision. Our preliminary results indicate that we may be able to apply multichannel quantum defect theory (MQDT) to uranium [12]. Indeed, it would be marked achievement if MQDT, which has been successful in explaining periodic perturbations and predicting level positions in light atoms [13], can provide a similar understanding of configuration interactions in the heaviest atomic systems.

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