Rise and Fall of the $4d^{10} \rightarrow 4d^9 4f$ Resonance in the Xe Isoelectronic Sequence

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The extreme-ultraviolet photoabsorption spectrum of a laser-produced lanthanum plasma has been recorded and found to contain a number of discrete features in the 130-eV region. These have been analyzed as $4d^{10} \rightarrow 4d^9 nf, np$ transitions in La^{3+}. We show that the $4f$ transition, which is expected to be the strongest, is not in evidence. The reason is that this resonance, after the collapse of the $4f$ wave function, has a large autoionization width. We conclude that the $4f$ orbital in Ba^{2+} is only partially collapsed, which settles a long-standing discussion of this point.

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The study of the extreme-ultraviolet (xuv) photoabsorption of extended isoelectronic sequences is a powerful investigative tool for the elucidation of inner-shell, two-electron, and photoionization processes in atoms and ions. In the case of ions the major experimental difficulty is that a suitable absorbing column must be produced and backlighted by an intense, synchronized continuum-emitting source. In the He I sequence, the extension of the photoabsorption technique to Li^+ was achieved[1] by means of a novel dual laser-plasma technique. In this method a Q-switched laser beam was divided into two parts; one part of the beam was brought to a line focus on a solid lithium target and produced the absorbing Li^+ column, the remainder of the beam was tightly focused on a tungsten target and produced an intense continuum-emitting background source. Subsequently[2,3] it was found that elements other than tungsten were suitable for xuv continuum generation over extensive energy ranges. The dual laser-plasma method was later applied to the study of a number of other ions along the He I,[4,5] Na I,[6] and Ne I[7] sequences.

An alternative technique, termed resonant laser-driven ionization, has been used to study the Xe I isoelectronic sequence,[8] in particular, Ba^{2+}. In this experiment an ionized column of ions was produced by irradiating a neutral-barium-vapor column with a powerful dye-laser beam tuned to the resonance transition of neutral Ba. This led to virtually 100% ionization of the atoms to Ba^+. To produce Ba^{2+} required the subsequent irradiation of the Ba^+ column by a second dye-laser beam tuned to the resonance transition in Ba^+. The results of the experiments showed discrete structures in the Ba^{++} $4d$ cross section near 100 eV. Most theoretical work[9-15] has focused on these results or on the expected behavior of the $4d$ photoabsorption cross section further along the Xe I sequence. Cheng and Froese Fischer[12] and Cheng and Johnson[13] have performed calculations for ions of this sequence up to Nd^{6+}; however, no experimental data exist past Ba^{2+} because of the difficulty in generating sizable populations of absorbing ionic species. The present paper reports the first experimental data on $4d$ photoabsorption for La^{3+}. The interpretation of the data requires a reevaluation of the $4f$ collapse along the Xe I sequence and, in particular, requires taking into account the impact of collapse on autoionization rates within the f series which has not been done before.

The xuv spectrum of neutral Xe has been studied extensively in the past. It is dominated by a wide $4d^{10} \rightarrow 4d^9 \epsilon f$ resonance, the structure and origin of which have been discussed intensively.[16] Two types of calculations have been used to interpret the results. One is a configuration interaction[17] (CI) or a random-phase approximation with exchange (alternatively a time-dependent local-density approximation[18]) calculation starting from the Hartree-Fock (HF) (or similar) wave function for the mean energies of the $4d^9 nf, \epsilon f$ series members, $\mathrm{HF}(E_{\mathrm{av}})$; the other type is a HF calculation of the $4d^9 nf, \epsilon f\ ^1P$ states, $\mathrm{HF}(^1P)$, which are the only ones that can be reached from the ground state in an LS approximation. The success of the latter method is based on the observation that the important interaction, which is incorrectly described in the $\mathrm{HF}(E_{\mathrm{av}})$ calculation, is the $4d$-$nf, \epsilon f$ exchange interaction in the ^1P state and this is taken into account in a $\mathrm{HF}(^1P)$ calculation. In Xe I, exchange is so strong in the ^1P state that the $4f$ orbital, and thus all higher bound orbitals, are pushed outside the $4d$ orbital. Consequently, the dipole matrix elements connecting the ground state with the $nf\ ^1P$ series members are small and very little intensity is found in the bound spectrum. On the other hand, the free ϵf elec-

tron has enough energy to surmount the potential barrier and the main absorption is found in a broad peak in the continuum. The situation is basically the same in the case of neutral Ba.

The absorption spectrum of Ba^{2+} is different. There is still a strong feature in the continuum but a major part of the absorption strength has moved into the bound region.[8] This has been interpreted as evidence for the collapse of the $4f$ wave function between neutral and twice-ionized Ba which would lead to better overlap between $4d$ and nf with larger dipole matrix elements as a consequence. With increasing ionization the calculations[12,13] predict that the oscillator strength will be concentrated in the $4d^{10} \rightarrow 4d^9 4f\,^1P$ transition with the result that basically only one very strong line should be observed in the bound region (see Fig. 2 in Ref. 12) and that the continuum absorption should be very weak.

The degree of collapse which occurs in Ba^{2+} has been the subject of discussion[8-13] because at least four equally strong resonances are observed. The most successful calculation has been published by Clark[15] who carried out a type of multiconfigurational HF calculation including spin-orbit interaction with some correlation in the initial and final states. This calculation was very successful in describing the experimental spectrum and we show that one reason for the good agreement is that for Ba^{2+} the $4f$ orbital is only partially collapsed in the $4f\,^1P$ state. Isoelectronically we show that reality (at least using a photographic plate for detection) is rather different from the prediction of one very strong resonance.

In the present experiment, the 1.5-J output of a Q-switched ruby laser was optically divided. A point focus was formed on either a hafnium or tungsten target to yield a hot plasma which acted as the source of background continuum while a line focus formed on an adjacent lanthanum target yielded a 5-mm-long absorbing ion column. The resulting spectra were recorded photographically, on a 2-m grazing-incidence spectrograph, with standing-wave-ratio plates. The spectrum obtained for lanthanum is shown in Fig. 1. Similar exposures were made for Ba.

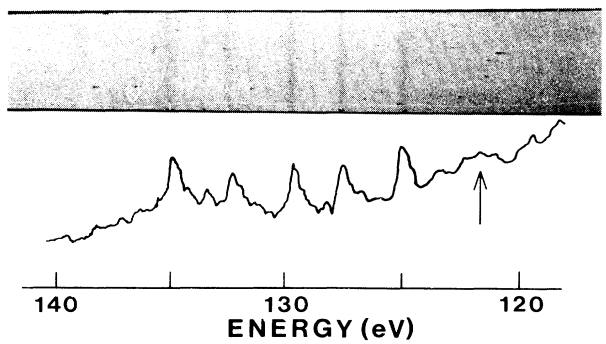

FIG. 1. The photographic absorption spectrum of the La plasma. Below is shown a densitometer trace. The predicted position of the $4f$ peak is indicated by the arrow.

Both spectra (Ba and La) were found to contain a number of discrete features which in the barium spectrum corresponded to the strongest of those previously observed[8] in the spectrum of Xe-like Ba^{2+}. This observation is not unexpected as the dominant ionization stages in laser-produced plasmas tend to have closed-shell configurations because of the sharp increase in energy required to ionize to the next stage. In similar absorption experiments on Mg, Al, and Si performed with the same experimental arrangement[7] the dominant absorbing species always was the Ne I–like ion. It is thus reasonable to assume that the predominant absorbing species in the present experiment is La^{3+}. To further check this point the focusing conditions on the lanthanum target were varied by changing both the lens type and the lens-to-target distance. In these experiments it was found that the discrete features displayed the same behavior; i.e., they either grew or diminished in intensity as a group.

To interpret the spectrum we have carried out calculations of the energy-level positions and intensities using the suite of programs written by Cowan.[19] The energy-level positions and oscillator strengths were determined in a CI calculation using a discretized continuum.[20] We made a calculation for Ba^{2+} in order to test the quality of the approach which we subsequently were going to apply to La^{3+}. A number of bound $4d^9 5s^2 5p^6 nf$ HF(E_{av}) and np functions, as well as continuum $4d^9 5s^2 5p^6 \epsilon f$ HF(E_{av}) functions, were used as basis states in an expansion which gave energy levels and oscillator strengths for the transitions $4d^{10} \rightarrow 4d^9 nf, np$ using a HF calculation for the ground state. Good agreement was obtained with the calculation due to Clark[15] as well as with experiment[8] with regard to both energy-level positions and intensities, keeping the accuracy of the photographic plate as an intensity detector in mind. The leading eigenvector components in the HF(E_{av}) basis are all rather small and, in particular, *no level has a large* $4f(E_{av})$ *(collapsed) component* [the lowest $f\,^1P$ level has a $4f(E_{av})$ component of less than 0.1]. One consequence is that no oscillator strength is particularly large. This can also be seen from the fact that the nominally weaker transitions to np states are of roughly the same strength. Another consequence will be discussed later.

Table I shows the results of the equivalent calculation for La^{3+} compared to our experimental results. The labels used in Table I are the largest LS component in the particular level. Many of these are much smaller than 50% and therefore have little significance. This can also be seen from the apparently random order of the higher $nf\,^1P$ labels (see also Ref. 15). The lowest $f\,^1P$ state here has a dominant $4f(E_{av})$ (collapsed) component of 50% with an associated oscillator strength of 4.0. This indicates that the interaction with the ϵf continuum is less important in La^{3+} and that a limited CI expansion, consequently, should be more accurate than in Ba^{2+}. We also note that the gf values are in quite good agree-

TABLE I. Identification of features in the La^{3+} spectrum. *LS* coupling is used to label the levels but most of the configuration labels have little significance (see text). Intensities are visual estimates. The calculations are described in the text. Only transitions with a gf value of more than 0.01 are included, where gf is the weighted oscillator strength.

Transition $4d^{10}\,^1S_0 \rightarrow 4d^9nl\,J=1$	E_{calc} (eV)	gf	FWHM (eV)	E_{obs} (eV)	Intensity	gf [a]
$4f\,^3D$	102.8	0.02	0.018			
$6p\,^1P$	117.3	0.01	0.004 [b]			
$4f\,^1P$	121.0	3.98	1.4	...		4.315 ($4f$)
$5f\,^3D$	125.7	0.88	0.36	125.1	10	
$7p\,^1P$	126.3	0.05	0.002 [b]	126.0 [c]	0–1	
$5f\,^1P$	128.2	0.76	0.31	127.6	8	1.297 ($5f$)
$7p\,^1P$	129.0	0.02	0.0005 [b]	128.8	1	
$6f\,^3D$	130.4	0.36	0.20	129.7	10	
$8p\,^1P$	130.4	0.60	0.22 [b]			
$7f\,^3D$	132.1	0.01	0.004	131.7 [c]	0–1	
$6f\,^1P$	133.0	0.51	0.25	132.5	8	0.591 ($6f$)
$8p\,^1P$	133.1	0.03	0.003 [b]			
$8f\,^1P$	134.0	0.32	0.16	133.65	6	0.321 ($7f$)
$9f\,^1P$	134.8	0.02	0.011			
$7f\,^1P$	135.2	0.16	0.086	135.25 [d]	4	0.194 ($8f$)
$10f\,^1P$	135.7	0.28	0.16		5	0.127 ($9f$)

[a] Reference 12; no spin-orbit interaction included. The configuration label is in parentheses.
[b] The decay of np basis states has not been included.
[c] Weak feature only observed on some plates.
[d] Feature possibly double.

ment with those determined in Ref. 12 using HF(^1P) wave functions (without spin-orbit interaction). Nevertheless, assuming the same accuracy in the energy-level predictions in La^{3+} as in Ba^{2+} we do not observe a strong feature at the position predicted for $4f\,^1P$ (see Fig. 1). However, if we assume that the transition to $4f\,^1P$ is not present, there is good agreement between our predictions and the observed transitions starting with $5f\,^3D$. Attempts to identify the lowest-observed resonance with $4f\,^1P$ do not lead to agreement with regard to either energy or oscillator strength for the observed features, so we are faced with the situation that the strong resonance predicted by us and by others apparently is absent on our plates.

Several potential explanations of this puzzle were explored. One was based on the observation that the $4f$ orbital, which in the beginning of the sequence is less strongly bound than $5p$, with increasing ionization becomes more tightly bound at which point the $4d^{10}5s^25p^6$ state ceases to be the ground state. We believe that this has not yet occurred for La^{3+} but we have carried out calculations which show that, even in the presence of a $4d^{10}5s^25p^54f$ state close to the ground state, the $4d^94f\,^1P$ resonance in La^{3+} would simply be distributed over a finite number of strong transitions which would still be observable.

Considering the experimental spectrum in Fig. 1, we noticed that the observed transitions have widths larger than the instrumental width. The final states $4d^95s^25p^6nf,np$ are far above the first ionization limit of La^{3+} which is associated with the $4d^{10}5s^25p^5$ configuration. We have therefore considered the autoionization widths of these resonances using the perturbation approach described by Cowan.[20] Previously Cheng and Johnson[13] considered the autoionization of those $4d^9(^2D_{3/2})nf$ levels for which decay to the $^2D_{5/2}$ threshold is possible, but these authors did not take into account the decays to the lower thresholds. The nonradiative decay from $4d^95s^25p^64f$ to $4d^{10}5s^25p^5\epsilon l$, say, is determined by the electrostatic $R^k(4f5p,4d\epsilon l)$ integral which can be large if $4f$ is collapsed, while the integrals associated with the decay of the higher nf resonances will be much smaller and only weakly dependent upon whether $4f$ is collapsed or not. The widths of the resonances have been estimated using the eigenvectors determined already in conjunction with R^k integrals connecting the bound nf basis states to the $5s^25p^5\epsilon l$ and $5s5p^6\epsilon l$ continua (decay to $5s^25p^44f\epsilon l$ continua was found to be less important). The results cannot be considered more than a first approximation to the real widths but since the largest interaction integral is due to the $4f(E_{av})$ component the main features of the calculation will probably be correct.

The calculated width of the $4f\,^1P$ state in La^{3+} (Table I) is between 1 and 2 eV. It should be pointed out that this calculation assumes that the interaction with the

continuum does not lead to an asymmetric, Beutler-Fano, line profile. If that assumption is wrong, and there are perhaps indications for the other resonances in Fig. 1 that this is the case, the intensity will be distributed over an even wider range than our calculation indicates. This makes it likely that the reason for the disappearance of the resonance is that its autoionization width has become so large that it is spread out over too extensive a wavelength range to make it visible on a photographic plate with the limited dynamic range.

It should be noted that the (collapsed) $4f$ HF(E_{av}) orbital in *both* Ba^{2+} and La^{3+} leads to autoionization widths of the same order of magnitude. The reason that the lowest $f\,^1P$ state in Ba^{2+} is narrow enough to be readily observed in absorption is thus that the $4f$ orbital in the ^1P state in Ba^{2+} is only slightly collapsed, which is reflected in the small $4f(E_{av})$ components in the bound levels mentioned earlier. This is one reason for the success of Clark's calculation[15] which does not include autoionization. In La^{3+} the $4f\,^1P$ orbital has collapsed further, with the result that the autoionization width has increased by a factor of around 20. Still, the fact that the $4f(E_{av})$ component in the lowest state is only 50% means that even here complete collapse in the ^1P state has not yet taken place. The very gradual collapse we propose agrees with the results of the calculations in Ref. 12.

As mentioned above, the difference in autoionization width occurs only for the lowest resonance ($4f\,^1P$) due to the difference in overlap between $4f$ and $4d$ for a collapsed and an uncollapsed $4f$ orbital. For the higher resonances there is no substantial difference in width when $4f$ collapses and thus only a slight increase in width between Ba^{2+} and La^{3+}. The complete results for the two ions will be published elsewhere.

Similar behavior along isoelectronic sequences can be expected in other cases of inner-shell excitation where $\Delta n = 0$. One example is $5d$ excitations in the actinides where $5f$ collapses. Here the electrostatic integral involved is $R^k(5d\epsilon l, 5fnl)$. A case where we do not expect a similar effect is the $2p \rightarrow 3d$ excitations in the Fe-group elements where the integral is $R^k(3l3l, 2p\epsilon l)$.

In conclusion, we have shown that the collapse of the $4f$ orbital in the Xe I isoelectronic sequence leads eventually to very large autoionization widths for the $4d^9 4f\,^1P$ resonance. This in turn leads to the "disappearance" of this resonance. Higher up in the isoelectronic sequence the degeneracy between $5p$ and $4f$ will change the appearance of the spectrum further.

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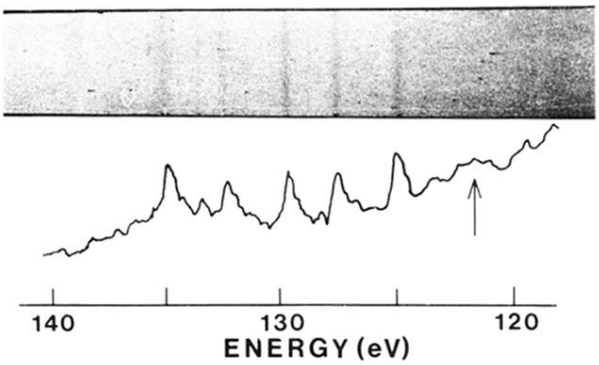

FIG. 1. The photographic absorption spectrum of the La plasma. Below is shown a densitometer trace. The predicted position of the $4f$ peak is indicated by the arrow.