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Role of autoionization in the near-threshold photoionization of argon and krypton metastable atoms*

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A molecular-beams apparatus is used in conjunction with a pulsed tunable uv laser to study the photoionization of argon and krypton $mp^5(^2P_{1/2})\ (m+1)s'$: $(^3P_0)$ and $mp^5(^2P_{3/2})\ (m+1)s$: $(^3P_2)$ metastable atoms in the wavelength range 3250–2690 Å. Major contributions to the ionization arise from excitation to $p^5(^2P_{1/2})nf'$ and $p^5(^2P_{1/2})np'$ levels which autoionize into the underlying $P_{3/2}$ continuum. Term values are presented for these levels and compared with those calculated by extrapolation of the lower levels of these series, whose term values are known from spectroscopic observations. The widths of the autoionizing peaks are discussed together with the relative transition probabilities.

Autoionization of high-lying *ns'* and *nd'* levels in argon and krypton excited optically from the $^1S_0$ ground state has already been reported.[1-3] In addition, electric quadrupole transitions from the ground state to nonautoionizing *np'* and *nf'* levels in argon have been observed.[4] In the present work excitation from the $^3P_{0,2}$ metastable levels has allowed a study of autoionizing *np'* and *nf'* levels in both argon and krypton.

The apparatus has been described elsewhere.[5,6] Briefly, a beam containing argon or krypton atoms in metastable $^3P_{0,2}$ states produced by electron impact is intersected at right angles by the output beam of a pulsed tunable uv laser. The resultant photoions are detected using a particle multiplier. A gating technique is used to distinguish these ions from those liberated at surfaces by scattered laser light and those arising from chemi-ionization in collisions between metastable atoms and residual gas in the system.

The radiation required to excite the transitions is obtained by frequency doubling the output of a tunable pulsed dye laser operating in the visible.[7,8] The uv laser is operated at a pulse repetition rate of 10 pulses/sec, a pulse power of several kilowatts and linewidth of ~0.7 Å. The wavelength determinations are made using a $\frac{1}{2}$-m Jarrel-Ash spectrometer, which was calibrated absolutely using a variety of spectral sources. The mean power and hence mean photon flux in the laser beam is measured using an Eppley thermopile.

The ion count rates, normalized to both unit photon flux and unit metastable atom density, are shown for argon in Fig. 1 and for krypton in Figs. 2 and 3, and are seen to display a series of sharp maxima. The ion production observed in the case of argon in the wavelength range 3070–2945 Å has been reported previously.[5] For brevity, the structure is interpreted here only in the case of krypton, since that in argon arises in a completely analogous manner. In Fig. 4 is shown an abbreviated term diagram for krypton which includes, in addition to the metastable levels and series limits, several *np'* and *nf'* terms. The resonances observed in Fig. 2 arise from transitions from the 5*s'* level to *np'* $J=1$ autoionizing levels. Those in Fig. 3 arise from transitions from the 5*s* level to upper *np'* $J=1$, 2 and *nf'* $J=2$, 3 levels. While the occurrence of *s*-*f'* transitions may at first glance appear surprising, they nonetheless obey the electric-dipole selection rules. However, *s'*-*f'* transitions are not observed because of the J selection rule.

Term values for the *np'* and *nf'* levels, obtained with reference to those of the known metastable levels, are listed in Tables I and II for argon and krypton, respectively. An uncertainty of ±8 cm^{-1} is present in each measurement owing in part to nonreproducibilities associated with the grating drive mechanism in the spectrometer and in part to the difficulty in tuning the laser more accurately to a given wavelength. Both these sources of error are essentially random. The major systematic error arises from the small uncertainty associated with the absolute calibration of the spectrometer. As a result the major errors in measuring the term values are random in nature.

It is interesting to compare the measured term values with those that may be derived by a quantum defect extrapolation of the lower members of the series. Term values for the higher members in a series are often obtained by a linear extrapolation of the known quantum defects of the lower terms using the Ritz formula[9]

$$\delta=\alpha+\beta T,$$

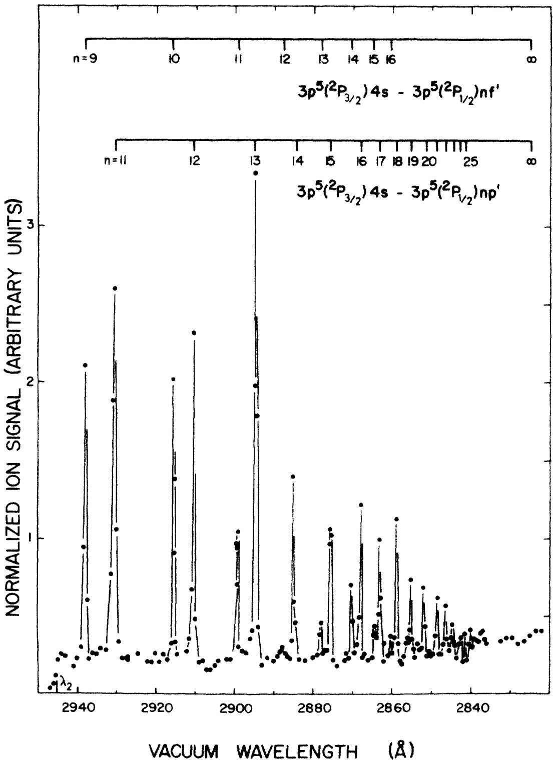

FIG. 1. Normalized argon-ion signal in the wavelength range 2950–2820 Å.

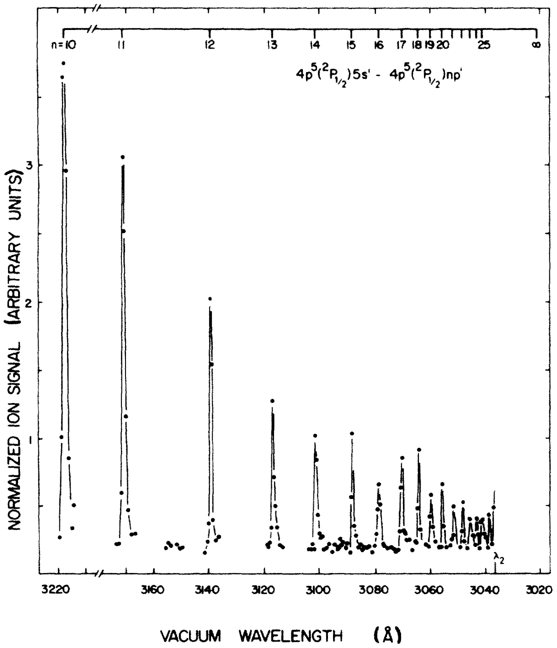

FIG. 2. Normalized krypton-ion signal in the wavelength range 3220–3035 Å.

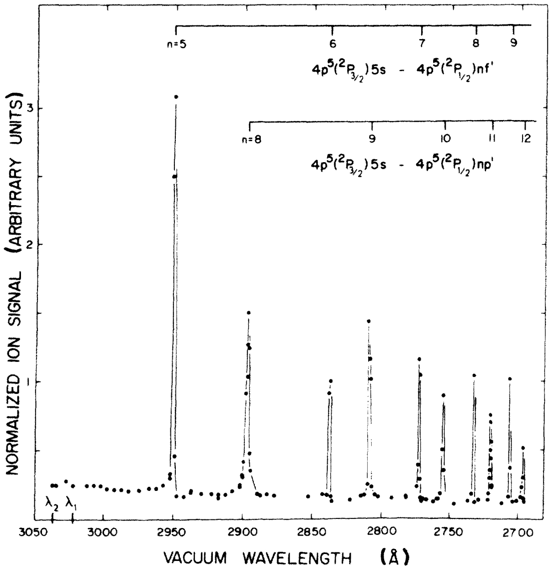

FIG. 3. Normalized krypton-ion signal in the wavelength range 3050–2690 Å.

where δ is the quantum defect, α and β are constants, and T is the absolute term value defined as the energy separation between the term of interest and the continuum. In the case of the rare gases, however, irregularities in the quantum defects for a given series are frequently observed.

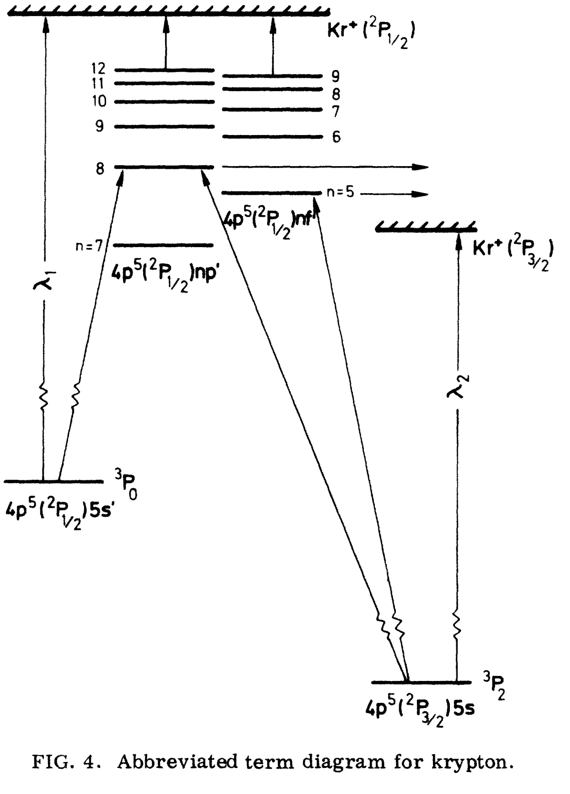

FIG. 4. Abbreviated term diagram for krypton.

TABLE I. Summary of argon term values.

	$3p^5(^2P_{1/2})np'$ Term values (cm^{-1})				$3p^5(^2P_{1/2})nf'$ Term values (cm^{-1})		
	Measured				Measured		
n	Excitation from $^3P_0$ level	Excitation from $^3P_2$ level	$np'[\frac{3}{2}]$ $J=1$[a]	Extrapolated[b] $np'[\frac{3}{2}]$ $J=1$	Excitation from $^3P_2$ level	$nf'[\frac{5}{2}]$ $J=3$[a]	Extrapolated[c] $nf'[\frac{5}{2}]$ $J=3$
4			107 131.76			121 654.32	
5			118 407.49			124 137.29	
6			122 609.76			125 483.16	
7			124 643.54			126 259.02	
8			125 783.8				126 822.4
9					127 181		127 183.4
10					127 437		127 441.5
11	127 273	127 269		127 275.4	127 636		127 632.6
12	127 508	127 503		127 509.0	127 774		127 777.9
13	127 686	127 686		127 683.5	127 891		127 891.0
14	127 812	127 813		127 817.2	127 982		127 980.7
15	127 926	127 920		127 921.9	128 049		128 053.1
16	128 010	128 011		128 005.5			128 112.3
17	128 068	128 070		128 073.2			128 161.4
18	128 128	128 123		128 128.8			128 202.5
19	128 169	128 168		128 175.1			128 237.3
20	128 212	128 211		128 214.0			128 267.0
21		128 249		128 247.0			128 292.6
22		128 273		128 275.3			128 314.7
23		128 298		128 299.7			128 334.1
24		128 323		128 320.8			128 351.0
25		128 340		128 339.4			128 366.0
26		128 356					128 379.3

[a] C. E. Moore, Natl. Bur. Stds. Circ. No. 476.

[b] Results of Ref. 5; typographical error incorrectly lists series as $np'[\frac{1}{2}]$ $J=1$.

[c] Series limit taken as 128 541.8 cm^{-1}.

These perturbations arise from interactions between series having the same parity and J^{10}. Linear series extrapolation can therefore only be carried out for these gases if either the terms in the series upon which the extrapolation is based are not significantly perturbed, and therefore conform to the Ritz formula, or if the perturbation of each level is calculated and the levels corrected before extrapolation. The extrapolated values, however, represent those appropriate to unperturbed higher terms and will be in error if the higher-term members are significantly perturbed.

The major perturbations of the p' series in both argon and krypton arise from interactions with the p series. This perturbation, as observed through the associated perturbation of the p series, for which many terms have been accurately determined spectroscopically, is large for the $p'[K=\frac{1}{2}]$ $J=1$ series but small for both the $p'[\frac{3}{2}]$, 1 and the $p'[\frac{3}{2}]$, 2 series. It should therefore be possible to obtain reliable term values for higher members in the series by extrapolating either the $p'[\frac{3}{2}]$, 1 or the $p'[\frac{3}{2}]$, 2 series. Since the $p'[\frac{3}{2}]$, 2 series may also interact with f and f' $J=2$ levels, it is to be expected that the more accurate results would be obtained by extrapolation of the $p'[\frac{3}{2}]$, 1 series. For argon several such levels are known accurately from spectroscopic data and the extrapolated term values for the $p'[\frac{3}{2}]$, 1 series, which are included in Table I, are seen to be in good agreement with those measured experimentally. In the case of krypton only two p' levels are known from spectroscopic data and as a result the extrapolation is subject to considerably more uncertainty. The results for the extrapolation of both the $p'[\frac{3}{2}]$, 1 and $p'[\frac{3}{2}]$, 2 series are included in Table II. It is seen that the terms of the $p'[\frac{3}{2}]$, 2 extrapolation are in better accord with the present experimental results than those of the $p'[\frac{3}{2}]$, 1 extrapolation. This would indicate that either the lower two levels of the $p'[\frac{3}{2}]$, 1 series are in fact perturbed or that only transitions to upper $p'[\frac{3}{2}]$, 2 or the almost energy coincident $np'[\frac{1}{2}]$, 1 levels occur.

In the case of the f' levels, both the quantum defects and level perturbations are much smaller than for the p' series. As in the p' case, it is possible to identify the f' series with the least perturbation, and calculate term values for the higher members of this series by extrapolation.

TABLE II. Summary of kryton term values.

	$4p^5(^2P_{1/2})np'$ Term values (cm^{-1})					$4p^5(^2P_{1/2})nf'$ Term Values (cm^{-1})		
	Measured			Extrapolated		Measured		Extrapolated
n	Excitation from $^3P_0$ level	Excitation from $^3P_2$ level	$np'\,[\frac{1}{2}]\ J=1$[a]	$np'\,[\frac{3}{2}]\ J=2$	$np'\,[\frac{3}{2}]\ J=1$	Excitation from $^3P_2$ level	$nf'\,[\frac{5}{2}]\ J=3$[a]	$nf'\,[\frac{5}{2}]\ J=3$
4							111 381.1	
5			97 920.05			113 866		113 868.4
6			108 515.0			115 219		115 219.8
7						116 040		116 034.2
8		114 494		114 496.0	114 463.0	116 564		116 562.5
9		115 585		115 593.6	115 573.4	116 925		116 924.5
10	116 273	116 270		116 274.3	116 261.2			117 183.3
11	116 729	116 732		116 725.7	116 716.7			117 374.8
12	117 046	117 048		117 040.4	117 033.9			117 520.3
13	117 274			117 268.5	117 263.7			
14	117 440			117 439.2	117 435.5			
15	117 575			117 570.2	117 567.4			
16	117 677			117 672.9	117 670.7			
17	117 762			117 755.0	117 753.2			
18	117 826			117 821.6	117 820.1			
19	117 876			117 876.4	117 875.2			
20	117 921			117 922.0	117 921.0			
21	117 961			117 960.4	117 959.5			
22	117 998			117 993.0	117 992.2			
23	118 026			118 020.9	118 020.2			
24	118 050			118 045.0	118 044.4			
25	118 074			118 065.9	118 065.4			

[a] C. E. Moore, Natl. Bur. Stds. Circ. No. 476.

These results are included in Tables I and II. It is important to note that because the quantum defects are very small, even large percentage changes in their values do not result in major modifications to the calculated term values. The calculated term values should thus be more reliable than those for the p' series and in all cases satisfactory agreement with the experiment is observed.

The $P_{3/2}$ continuum, in which the autoionizing levels are embedded, corresponds to the unquantized orbits of free electrons having the same parity and total angular momentum J as the series of discrete levels to which it forms an extension. Since autoionization results from interactions between the discrete np' or nf' states and this continuum, it is anticipated that series which interact strongly in the discrete-level region will also interact strongly with the continuum. Since the p'-p interaction, as observed through level perturbation, is greater than the f'-f interaction, it is to be expected that the lifetime of the p' levels against autoionization will be less than that for f' levels. Thus the widths of the p' autoionizing peaks should be greater than those of the f' levels. The measurements appear to confirm this, although it is not possible to accurately determine the widths or heights of the resonance peaks because they are so narrow. Nonetheless the full width at half-maximum of the widest peak is of the order of 1.5 Å (18 cm^{-1}), although this must be considered an upper bound because of the 0.7-Å linewidth of the laser. The lifetime of all the p' and f' levels against autoionization must therefore be longer than 2×10^{-12} sec. This relatively long lifetime suggests only a weak interaction of all p' and f' levels with the continuum. The widths of the autoionizing peaks corresponding to a given series are also observed to decrease as the principal quantum number increases. This is to be expected because the interaction with the $P_{3/2}$ continuum will be greatest near threshold, since that is where the density of the continuum is at a maximum.[10]

Several points concerning the strengths of the various transitions in krypton are worth comment. First, the probability for a transition to a given upper np' level from the $^3P_0$ level is typically a factor of 3 greater than that for the corresponding transition from a $^3P_2$ level, assuming the two metastable levels to be populated in the ratio of their statistical weights. The transition probabilities for excitation of f' and p' levels having the same n from the $^3P_2$ level are comparable. In argon there is a marked anomaly in the peak heights of both the p' and f' series in the vicinity of 2890 Å. Similar line-strength anomalies have been observed[4] in Rydberg series excited from the argon ground state and are thought to originate in perturbations caused by other levels.

It is possible to determine an upper bound to the absolute cross sections for direct photoionization of metastable argon and krypton atoms into their respective continua. An absolute cross-section measurement would require the determination of the number density of the metastable atoms illuminated by the laser beam, which may be derived from measurements of the absolute flux of the metastable atoms together with their velocity distribution.[11] To measure the absolute flux it is necessary to know the absolute secondary electron-ejection coefficient γ for the surface used as detector. At the present time, however, only an upper bound to the values of γ for argon and krypton metastables may be obtained[12] and the corresponding upper bounds to the absolute cross sections for photoionization of Ar$({}^3P_{0,2})$ and Kr$({}^3P_{0,2})$ atoms at threshold are 1.1×10^{-18} and 4.9×10^{-19} cm^2, respectively. (The gas-cell technique[12] is based on the assumption that destruction of metastables in gas-phase collisions always results in ion production. For argon and krypton metastable atoms the quenching gas is necessarily molecular, and de-excitation of metastable atoms in collisions resulting in dissociation or excitation[13] rather than ionization is possible. The effect of such collisions is to permit only an upper bound to γ to be obtained.) The ion production observed in Fig. 2 in regions remote from autoionizing peaks results from direct transitions from the ${}^3P_0$ level into the $P_{3/2}$ continuum.

The present results demonstrate that in the near threshold region an important contribution to the ion production results from autoionization. Similar effects are to be expected in ion or neutral species of similar configuration and such a contribution to the ion production must be taken into account when considering ion-generation rates in and radiation transmission through plasmas.

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