(4c), which can be written more specifically as,

$$J_\varphi(1)=r_1^{-1}\int_0^{r_1} dr_2 r_2^2\rho(2)+\int_{r_1}^{\infty} dr_2 r_2\rho(2), \quad \text{(A1)}$$

where ρ is the radial charge distribution for the s orbital. Upon inserting the expansion [Eq. (18)] for the Hartree-Fock orbital, ρ becomes

$$\rho(2)=\sum_{n,\alpha}\sum_{n',\alpha'} a_{n\alpha}a_{n\alpha}'(2\alpha)^{n+\frac{1}{2}}(2\alpha')^{n'+\frac{1}{2}} \times[(2n)!(2n')!]^{-1/2} r_2^{n+n'-2}e^{-(\alpha+\alpha')r_2}. \quad \text{(A2)}$$

Carrying out the indicated integrations, (A1) becomes

$$J_\varphi(1)=\sum_{n\alpha}\sum_{n'\alpha'} a_{n\alpha}a_{n\alpha}'(2\alpha)^{n+\frac{1}{2}}(2\alpha')^{n'+\frac{1}{2}} \times[(2n)!(2n')!]^{-1/2}(n+n')!(\alpha+\alpha')^{-n-n'-1} \times\left\{\frac{1}{r_1}-\frac{1}{r_1}e^{-(\alpha+\alpha')r_1}-\frac{\alpha+\alpha'}{n+n'}e^{-(\alpha+\alpha')r_1} \times\sum_{k=0}^{n+n'-2}\frac{(n+n'-k-1)(\alpha+\alpha')^k}{(k+1)!}r_1^k\right\}. \quad \text{(A3)}$$

Matrix elements for this operator are clearly simply multiple sums over the usual helium-like integrals.

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Observed and Predicted New Autoionized Energy Levels in Krypton, Argon, and Xenon*

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The absorption spectrum of argon and krypton has been investigated between 400–600 Å. Discrete structure is observed which can be related to the excitation of an inner s electron. Configuration interactions between the discrete excited levels and the overlapping ionization continuum leads to autoionization of the energy levels, as evidenced by the fact that the measured photoionization yield within the discrete structure is 100%. The first member of the series is observed at 466 Å for argon and 497 Å for krypton with a predicted value of 593 Å for xenon. The Rydberg series $\nu=235\,832-R/(n-1.53)^2$, $n=4, 5, \cdots$, etc., describes the argon data while similar series are predicted for krypton and xenon with quantum defects equal to 2.53 and 3.53, respectively, and using the appropriate term value for their respective N_1 and O_1 absorption edges.

THE photoionization cross sections of argon and krypton have been measured between 400–560 Å. In both gases discrete structure is observed superimposed on the photoionization absorption continuum. The structure in argon can be identified with the new autoionized energy levels recently observed spectroscopically by Madden and Codling,[1] while that of krypton has not previously been reported. The structure in the krypton photoionization cross sections is assumed also to be due to autoionized energy levels, since the photoionization yields for the discrete structure in both argon and krypton were measured and found to be 100%.

The anomalous nature of the autoionized lines in showing a decrease in absorption with no accompanying increase is apparently allowed in the Fano theory of autoionization.[2]

The cross-section measurements were made on a 1/2 M Seya-type vacuum monochromator with a 2.5-Å band pass. The light source consisted of a high-voltage repetitive spark discharge in argon which produced an extremely dense line spectrum above 400 Å. The absorption cell consisted of two ionization chambers in series and of identical lengths d. The absorption coefficient μ is then given by

$$\mu=\ln(i_1/i_2)/d,$$

where i_1 and i_2 are the ion currents produced, respectively, in the two-ion chambers. A detailed discussion of this technique is described in another paper.[3] The gas pressure was varied from 0.05–0.5 Torr and the effective absorption length d was 10 cm. The major advantage of this technique in the measurement of absorption coefficients is that i_1 and i_2 (and hence μ) are measured simultaneously and are, therefore, independent of any changes in light source intensity.

The photoionization cross sections, reduced to STP, are shown in Figs. 1 and 2 for argon and krypton, respectively. With the exception of the discrete structure the cross sections are pressure-independent (±5%) over a pressure range of 0.05–0.5 Torr.

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[1] R. P. Madden and K. Codling, Phys. Rev. Letters **10**, 516 (1963).
[2] U. Fano, Phys. Rev. **124**, 1866 (1961).
[3] J. A. R. Samson, J. Opt. Soc. Am. **53**, 507 (1963).

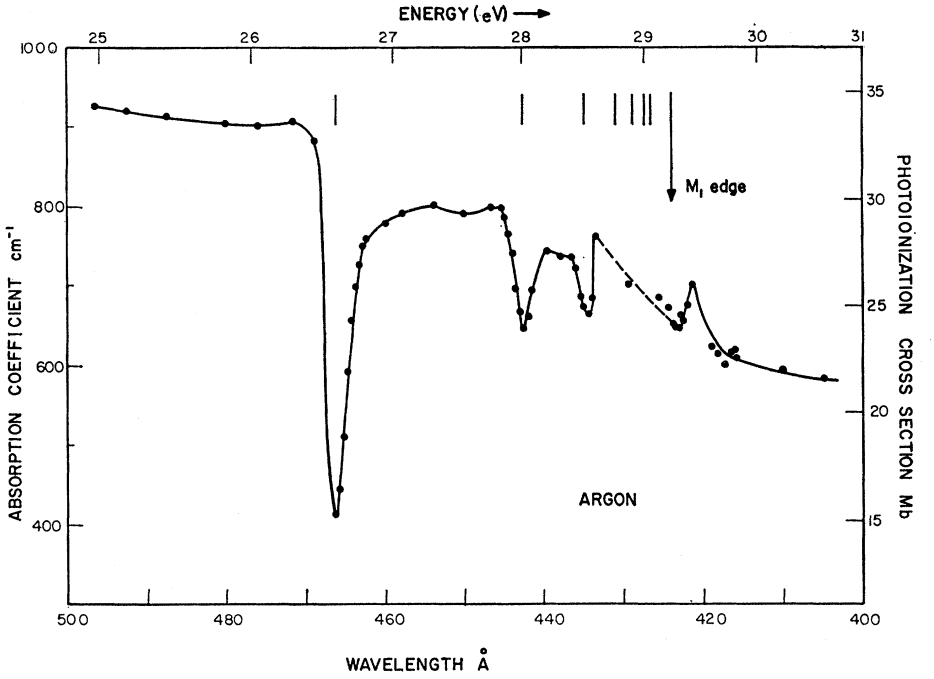

FIG. 1. Photoionization cross sections for argon between 400–500 Å. The vertical lines represent the positions of the autoionized series reported in Ref. 1, while the vertical arrow indicates the position of the M_1 edge due to the removal of an s electron.

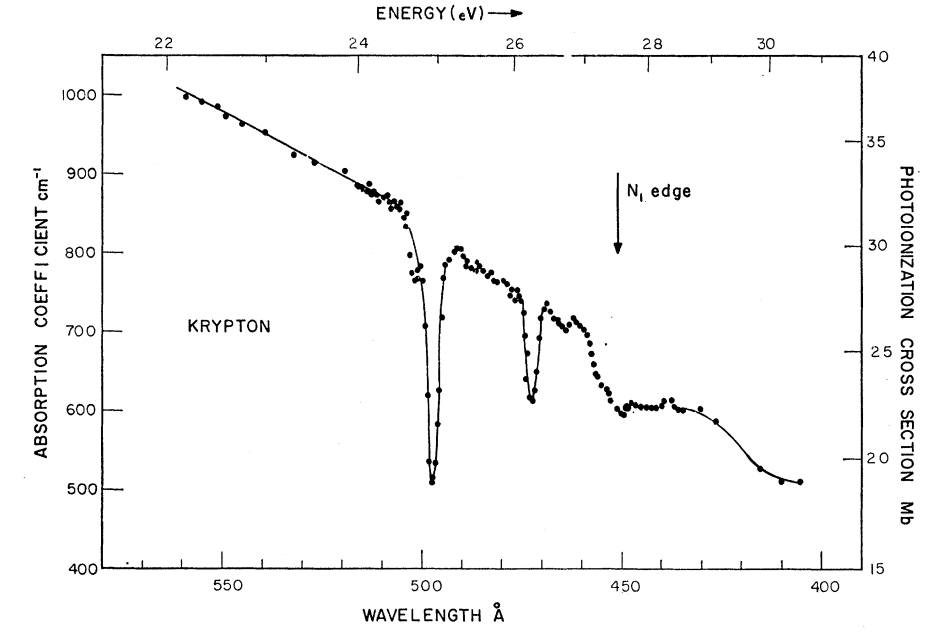

FIG. 2. Photoionization cross sections for krypton between 400–460 Å. The vertical arrow indicates the position of the N_1 edge due to the removal of an s electron.

There exist very little data on the photoionization cross sections of krypton and argon between 400–500 Å, with the exception of the work on argon by Po Lee and Weissler[4] who used photographic techniques to measure the cross sections. Where data exist there is agreement within 10%.[5,6]

[4] Po Lee and G. L. Weissler, Phys. Rev. **99**, 540 (1955).
[5] N. Wainfan, W. C. Walker, and G. L. Weissler, Phys. Rev. **99**, 542 (1955).
[6] A. Pery-Thorne and W. R. S. Garton, Proc. Roy. Soc. (London) **76**, 833 (1960).

The vertical lines in Fig. 1 represent the positions of the autoionized lines in argon discovered by Madden and Codling using the continuum radiation from a 180-MeV synchrotron.[1] It can be seen that the discrete absorption structure coincides exactly with the first three terms of their series. In the present work these lines appear at 466, 442.8, and 434.8 Å. There is an uncertainty of ±0.5 Å in the wavelength determination. The linewidths shown here are instrumental, reflecting the 2.5-Å bandpass of the monochromator. The vertical

TABLE I. Observed wave numbers in argon for the transition $3s^23p^6-3s3p^6np$ compared to the calculated values given by $\nu=235\,832-R/(n-1.53)^2$.

n	ν_{obs}	ν_{calc}
4	214 500	217 845
5	225 700	226 718
6	229 900	230 340
7	232 000	232 164
8	233 200	233 211
9	233 900	233 865
10	234 300	234 302
11	234 600	234 608

arrow represents the M_1 edge at 424 Å as obtained from spectroscopic data.[7] The experimental value of 422 Å is in good agreement with this value.

The autoionized lines observed in krypton appear at 471.8 and 497 Å with the suggestion of one at 464 Å. A sudden discontinuity in the curve occurs at 449 Å, in good agreement with the spectroscopic value of 450.5 Å for the N_1 edge of krypton,[8] represented by the vertical arrow in Fig. 2.

It seems likely that the autoionized lines in argon and krypton are due to the excitation of the inner s electron terminating with its ejection at the M_1 and N_1 edges, respectively. If this is the case, the following Rydberg series for argon can be fitted to the data of Ref. 1 and to the first three terms of the present work.

$$\nu=235832-R/(n-1.53)^2 \quad n=4, 5\cdots, \text{etc.}$$

TABLE II. Observed quantum defects of the rare gases compared to those of the alkali metals. Numbers in italics indicate predicted values.

	Quantum defects								
Term	Ne[a]	Na	Ar[b]	Ar[a]	K	Kr[b]	Rb	Xe	Cs
$3p$	0.86	0.883	...	...	...	...	...	...	...
$4p$	0.85	0.867	1.73	1.73	1.77	...	...	...	...
$5p$	0.8	0.862	1.7	1.7	1.74	2.7	2.71	...	...
$6p$	0.8	0.860	1.7	1.7	1.73	2.7	2.67	*3.67*	3.65
$7p$	0.6	0.859		1.6	1.72	...	2.66	...	3.60
$8p$	0.6	0.858		1.6	1.72	...	2.66	...	3.59
				...		...		...	
				...		...		...	
∞				*1.53*		*2.53*		*3.53*	

[a] These values were deduced from an absorption spectrum in Ref. 1. The accuracy in the quantum defect for the first term is approximately ±0.01, however, for higher terms the inaccuracies increase to probably as much as ±0.1.
[b] Present work.

[7] C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards, Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. I.
[8] C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards, Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1952), Vol. II.

Table I compares the observed wave numbers to those calculated from the above series. The observed data were obtained from measurements made on an enlarged photograph, taken from Ref. 1, and, thus, are not so precise as their original data.

In order to fit a Rydberg series to the krypton data and thereby predict the higher terms of the series, the following system was adopted: If we assume that the first observed term in krypton is indeed the first member of the series $4s^24p^6-4s4p^6np$, we can then determine the quantum defect for $n=5$ and 6. Comparing these values with those deduced from Ref. 1 and also to the alkali metals we might expect to find a relationship between the various quantum defects enabling us to predict a quantum defect for the higher members of the krypton series. These quantum defects are tabulated in Table II. It can be seen that there is a very striking relationship, not only in the quantum defects between the rare gases but also compared to the alkali metals. The main features are (i) that the quantum defect increases approximately by unity in steps going from neon to argon to krypton and (ii) the quantum defect of a rare gas is essentially equal to that of the alkali metal next to it in the periodic table and whose final-state transition is the same as that of the rare gas. The similarity appears reasonable since we are essentially comparing the binding energies of similar electrons in closely related atoms. The quantum defect for the rare gases, however, does vary more rapidly than that of the alkali metals, probably due to the interaction between the discrete states and the continuum. Since the quantum defects in argon and krypton differ by unity in the first two terms we will assume this difference continues for higher members and thus predict the following Rydberg series for krypton,

$$\nu=221\,917-R/(n-2.53)^2 \quad n=5, 6\cdots, \text{etc.}$$

Similarly, we should expect from (i) above that the transition $5s^25p^6$-$5s5p^66p$ in xenon would have a quantum defect of 3.7 and from (ii) a value of 3.65. Assuming a mean value of, say, 3.67, the predicted term level would be approximately at 168 500 cm^{-1} (593 Å). Following the same reasoning as for krypton, the higher terms in xenon are predicted to follow the Rydberg series,

$$\nu=188\,708-R/(n-3.53)^2 \quad n=6, 7\cdots, \text{etc.}$$

A search for this series is currently underway.

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