PHYSICAL REVIEW VOLUME 109, NUMBER 6 MARCH 15, 1958

Emission Lines from Preionized Levels in Krypton and Xenon*

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(Received November 22, 1957)

In strong rare-gas discharges at relatively high pressures many hitherto unrecorded lines appear which are classified as transitions from preionized p' and f' levels to normal stable levels. Twenty-four such lines were found in the spectrum of Kr I and thirty in the spectrum of Xe I. The intensity of these lines may be used to measure the ion density.

PREIONIZED levels of atoms, that is stable or semistable levels above the first ionization potential, are of particular interest, but are relatively little known.[1] Such levels may be sharp when the interaction with the ionization continuum is negligible or moderately diffuse or so diffuse as to be unrecognizable when the interaction is large. Examples are known from elements with more than one valence electron such as calcium, strontium, barium, mercury, and copper.

The transitions to and from many of these levels are distinguished from other lines by their diffuseness. This can best be observed in the absorption spectrum. In emission under normal conditions the diffuse lines are absent or extremely weak. The lifetime of such preionized states is short compared to 10^{-8} sec so that atoms in these states will be ionized rather than emit light. Lines from these states are strengthened in emission if the electron density is large so that recombinations take place frequently.[2] The intensity of emission lines from preionized states must, therefore, be a measure for the electron density which in neutral plasmas is equal to the ion density. While there are several other methods for the determination of ion densities, none of these is ideal and the development of an independent method is very desirable.

The first prerequisite is the identification of preionized levels in gases which can be excited in a simple and reproducible way. Metal vapors are not very suitable for this, but the rare gases present very favorable conditions. The heavy rare gases have the two lowest levels of the ion, $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$, sufficiently separated so that a considerable number of preionized levels can be expected between the two ionization limits. These will not be very different in energy from the ordinary levels so that the lines coming from them will lie in the same region of the spectrum.

The present paper deals with lines from preionized levels in krypton and xenon. None of these levels were known previously. Beutler,[3] on the other hand, has observed diffuse lines in absorption which have the preionized states ns_{01}' and nd_{01}' as upper states. We have not observed any lines originating from these levels in emission, presumably because they would be too weak and too broad.

NOTATION

As proposed by Racah,[4] a state in a rare gas atom is characterized by the total quantum number n of the excited electron, by its orbital angular momentum l (expressed as usual by the symbols s, p, d, f, etc.), the intermediate quantum number K (angular momentum of the atom minus the spin of the excited electron), and the total angular momentum J. The quantities $K-\frac{1}{2}$ and J are added as subscripts to the term symbol. (The integer $K-\frac{1}{2}$ is used instead of K for ease in writing.) A prime is attached to the symbol if the state

TABLE I. Lines from preionized levels in krypton.

λ(A)	ν(cm⁻¹)	Classification	$\mathrm{Log}_{10}I$[a]	Half-width (cm⁻¹)	Upper level (cm⁻¹)
5593.5	17 872	$4d_{00}$-$8p'$	1.8	15.5	114 644
5699.1	17 542	$4d_{01}$-$8p'$	1.6	16	114 628
5904	16 933	$4d_{11}$-$8p'$	3.32	20	114 622
6096	16 400	$4d_{33}$-$8p_{12}'$	2.04	9 ?	114 627
6361.1	17 766	$4d_{22}$-$8p'$	2.8	8.3	114 634
5342.5	18 713	$4d_{00}$-$9p'$		7.2	115 485
5636.961	18 388	$4d_{01}$-$9p$	1.89	5.0	115 474
5800.0	17 237	$4d_{33}$-$9p_{12}'$		5.5	115 464
5130.5	19 486	$4d_{00}$-$10p'$	2.19	4.5	116 258
5543	18 036	$4d_{33}$-$10p_{12}'$	2.23	4.7	116 263
5744.8	17 402	$4d_{22}$-$10p'$	1.8	5.1	116 270
5815.7	17 190	$4d_{23}$-$10p'$	2.6	5.5	116 270
5956.4	16 784	$4d_{01}$-$5f_{22}'$	2.24	2.2	113 870
6178.711	16 180	$4d_{12}$-$5f'$	2.93	2.6	113 869
6391.729	15 641	$4d_{33}$-$5f'$	2.24	2.4	113 868
6664.993	15 000	$4d_{22}$-$5f'$			113 868
5513.5	18 132	$4d_{01}$-$6f_{22}'$	1.83	1.8	115 218
5739.023	17 420	$4d_{34}$-$6f'$	2.24	3.7?	115 218
6313.8	16 352	$4d_{22}$-$6f'$	1.79	2.3	115 220
6194	16 140	$4d_{23}$-$6f'$	1.93	2.0	115 220
5278.859	18 949	$4d_{01}$-$7f_{22}'$	1.71	3.1	116 035
5448.3	18 349	$4d_{12}$-$7f'$	2.71	5.0	116 038
5481.138	18 239	$4d_{34}$-$7f'$			116 037
5614.0	17 808	$4d_{33}$-$7f'$	1.5	2.2	116 035

[a] I_1 photoelectrically measured intensities.

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* Work carried out with support of the Office of Ordnance Research of the U. S. Army.

[1] A. Shenstone, Phys. Rev. **38**, 873 (1931); H. E. White, Phys. Rev. **38**, 2016 (1931); see also the discussion in E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), p. 369.

[2] C. W. Allen, Phys. Rev. **39**, 42–55 (1932).

[3] H. Beutler, Z. Physik **93**, 177 (1935).

[4] G. Racah, Phys. Rev. **61**, 537 (1942); see also Condon and Shortley, reference 1, p. 301.

TABLE II. Lines from preionized levels in xenon.

λ(A)	ν(cm^{-1})	Classification	I_0[a]	Upper level (cm^{-1})
4123.55	24 244.1	$6s_{01}'$-$4f_{22}'$	10	101 429.7
4662.26	21 442.8	$5d_{01}$-$4f_{22}'$	6	101 430.0
4737.49	21 102.3	$5d_{12}$-$4f'$	6	101 425.6
5127.24	19 498.3	$5d_{22}$-$4f'$	6	101 424.3
7762.15	12 879.5	$6d_{01}$-$4f_{22}'$	4	101 429.8
7860.96	12 717.6	$6d_{12}$-$4f'$	20	101 426.6
10323.9	9 683.5	$5d_{23}'$-$4f_{22}'$	20	101 430.6
3737.81	26 746.0	$6s_{01}'$-$5f_{22}'$	5	103 931.6
4175.17	23 944.4	$5d_{01}$-$5f_{22}'$	6	103 931.6
4235.03	23 606.0	$5d_{12}$-$5f'$	15	103 929.3
4354.59	22 957.8	$5d_{33}$-$5f'$	6	103 928.7
4543.99	22 001.0	$5d_{22}$-$5f'$	6	103 927.0
6568.39	15 220.2	$6d_{12}$-$5f'$	30	103 929.2
6708.25	14 902.9	$6d_{33}$-$5f'$	3	103 928.3
6808.12	14 684.3	$6d_{22}$-$5f'$	5	103 928.1
7192.42	13 899.7	$6d_{11}$-$5f_{22}'$	4	103 932.4
7825.55	12 775.1	$5d_{22}'$-$5f'$	30	103 928.3
8009.59	12 481.6	$5d_{12}'$-$5f'$	30	103 929.6
(8206)	(12 182)	$5d_{23}'$-$5f'$	masked by 8206.336	
8469.55	11 803.8	$7d_{01}$-$5f_{22}'$	10	103 932.6
4004.55	24 964.6	$5d_{12}$-$6f'$	10	105 287.9
4279.16	23 362.5	$5d_{22}$-$6f'$	2	105 288.5
6029.78	16 579.8	$6d_{12}$-$6f'$	15	105 288.8
6230.81	16 044.9	$6d_{22}$-$6f'$	4	105 288.7
7072.44	14 135.5	$5d_{22}'$-$6f'$	30	105 288.7
7222.64	13 841.5	$5d_{12}'$-$6f'$	20	105 289.5
7382.57	13 541.7	$5d_{23}'$-$6f'$	30	105 288.8
3877.20	25 784.5	$5d_{12}$-$7f'$	2	106 107.8
6684.79	14 955.2	$5d_{22}'$-$7f'$	30	106 108.4
6961.10	14 361.6	$5d_{23}'$-$7f'$	20	106 108.7
6712.93	14 892.5	$5d_{23}'$-$8f'$	3	106 639.6

* I_0, estimated intensities.

belongs to a series converging to the excited level $^2P_{\frac{1}{2}}$ of the ion. All preionized levels must therefore be primed levels. (Example $5f_{23}'$:$n=5$, $l=3$, $K=2\frac{1}{2}$, $J=3$.)

EMPIRICAL DATA

Lines from broadened preionized levels should have negligible intensities in discharges at low pressure but should be strengthened greatly in strong discharges at high pressures where the electron density is high. For this reason the spectra of a microwave discharge in krypton[5] at 35-mm pressure and in xenon[6] at 16-mm pressure were examined. Numerous new lines were observed and measured. Under these conditions most lines are greatly broadened, and accurate wavelength measurements are not possible. Moreover the continuous background is strongly developed and weak diffuse lines do not appear clearly above the background on photographs of the spectrum. They are much more easily seen on photoelectric traces. The wavelengths could only be obtained roughly from these traces and cannot claim high accuracy. A few of the lines persisted in a krypton discharge at 1.6-mm pressure. Their wavelengths are listed to three decimal places in Table I.

The xenon lines in Table II were all obtained from 21-ft grating plates. They are absent in a low-pressure discharge.

ANALYSIS

The preionized nf' levels can be found by making use of a relation pointed out by Edlén[7]: $nf'=\frac{1}{3}(2nf_4+f_3)+\Delta\nu'$, where $\Delta\nu'$ is the difference between the two ionization limits.[8] $\Delta\nu'=5371.0$ cm^{-1} for krypton $\Delta\nu'=10\,537.0$ cm^{-1} for xenon. There should be four nf' levels for each $n'(f_{22}'f_{23}'f_{33}'f_{34}')$ which will, however, be so close together that they cannot be separated in the presence of the preionization broadening. (The total separation for $4f'$ in krypton where the levels are sharp is 3 cm^{-1}. It should be less for higher n.) We can, therefore, usually designate the upper level simply by nf'. If there is splitting, the f_{22}' level must be expected to be separated from the others.[8]

The f' levels should combine strongly with the known nd and nd' levels and less strongly with ns' and ns. Tables I and II give the observed lines. From their frequencies the empirical values of energy levels may be found (listed in the last column) and compared with the computed values. Table III shows that the agreement is excellent when one takes into account the broadness of the lines. Only f_{22}' can combine with levels having $J=1$. For xenon the $4f_{22}'$ and $5f_{22}'$ levels lie definitely above the average of the unresolved $4f'$ and $5f'$ levels respectively (see Table II).

Table I gives transitions from the $8p'$, $9p'$, $10p'$ levels of krypton to $4d$ levels where the upper levels are clearly identified by their relative position with respect to the f' levels. The corresponding lines in xenon have not yet been identified. Possibly they are too broad for easy recognition.[9]

The observed half-widths of the preionized krypton lines are listed in Table I. As under the prevailing experimental conditions the final levels have negligible widths,[5,6] the values listed are the half-widths of the levels. The half-widths of the nf' levels are not very different from those of the higher nf levels (for instance 1.99 and 3.16 cm^{-1} observed for $6f$ and $7f$, respectively). Very little can therefore be said about the interaction of these levels with the ionization continuum.

On the other hand, the np' levels show a much greater width than the corresponding np levels; moreover, the half-widths decrease with increasing energy which is the opposite variation from that observed for the stable levels but which was also found for the s' and d' levels.[3] We can, therefore, state with confidence that the width of the p' levels is largely determined by

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[5] For further details see Johns Hopkins Spectroscopic Report No. 14, 1957 (unpublished).

[6] For further details see Johns Hopkins Spectroscopic Report No. 12, 1955 (unpublished).

[7] Private communication; see B. Edlén, *Handbuch der Physik* (Springer-Verlag, Berlin, to be published), Vol. 27.

[8] G. H. Shortley and B. Fried, Phys. Rev. **54**, 749 (1938).

[9] Possibly two previously unclassified lines[6] of xenon may have the following identification: 21 880 cm^{-1}, $6s_{01}'$-$7p_{12}'$; 25 644 cm^{-1}, $6s_{01}'$-$8p_{12}'$.

the shortened half-life because of interaction with the ionization continuum.

So far we can only say the lines coming from preionized levels are very much weakened at low pressures. The quantitative relationship between their intensity and the electron density remains to be determined.

A few words should be said about the completeness of our present knowledge of the Kr I and Xe I spectra. All types of predicted levels have now been found. The new p' and f' levels cannot be expected to combine with the ground state because of the parity selection rule and this explains their absence in the absorption spectrum. As was mentioned before, the s' and d' levels observed in the far ultraviolet absorption are probably so broad that transitions from them will only contribute to the continuous emission spectrum. The p' levels in xenon have not yet been found definitely. The levels to be expected, p_{11}', p_{01}', p_{12}', p_{00}' in the order of increasing energies, are probably sufficiently separated to locate them individually. Unfortunately, the levels are so broad and the measurements so inaccurate that at the present time nothing can be said about the individual levels.

TABLE III. Agreement between calculated and observed f' levels.

	Krypton levels (cm^{-1})		Xenon levels (cm^{-1})		
	calc	obs	calc	obs nf'	obs nf_{22}'
$4f'$	111 378.6	111 380.2[a]	101 426.3	101 425.3	101 429.8
$5f'$	113 867.3	113 868	103 929.7	103 928.7	103 931.9
$6f'$	115 219.2	115 220	105 290.3	105 288.7	
$7f'$	116 033.8	116 037	106 110.1	106 108.3	
			106 641.7	106 639.6	

[a] Average of the four separated nonpreionized levels. See *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1952), Vol. II.

ACKNOWLEDGMENT

We are greatly indebted to Professor B. Edlén for his help and advice.

PHYSICAL REVIEW VOLUME 109, NUMBER 6 MARCH 15, 1958

Excitation Function for $Fe^{56}(n,p)Mn^{56}$†

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(Received November 18, 1957)

The relative cross section for $Fe^{56}(n,p)Mn^{56}$ has been measured by an activation method for neutron energies of 3.4 to 8.2 and 12.4 to 17.9 Mev, and normalized to the previously known value of 110±10 mb at 14.3 Mev. The cross section rises above the minimum detectable value of 0.2 mb at about 4.5 Mev, reaches a maximum of 116 mb at 13.5 Mev, and decreases to 62 mb at 17.9 Mev. The experimental results are compared with the predictions of statistical theory; the fit, although good in the vicinity of maximum yield, is poor at lower energies, the predicted yield being considerably too small. Cross sections for $Fe^{54}(n,2n)Fe^{53}$ were also roughly determined at 16.9 and 17.9 Mev.

INTRODUCTION

THE excitation function of the reaction $Fe^{56}(n,p)$ Mn^{56} is of interest from the various standpoints of fast neutron detection, reactor design, and nuclear theory. This reaction, with an energetic threshold of 2.9 Mev,[1] results in beta activity with a convenient half-life of 2.576 hours.[2] This paper reports activation measurements of the relative yield of the reaction at various neutron energies in the range from 3.4 to 17.9 Mev. The yield may be put on an absolute basis by normalization to the value 110±10 mb at 14.3 Mev, an average[3] of the results reported by Forbes[4] and by Paul and Clarke.[5]

EXPERIMENTAL PROCEDURE

The excitation function was determined by placing as many as 15 iron samples at various angles around d-D or d-T neutron sources, irradiating them simultaneously for about 2 hours, and measuring the induced Mn^{56} activities. Since the neutrons produced by these sources have energies varying rapidly with angle, a wide energy range can be covered by a few irradiations. In order to obtain relative cross sections for the energy range covered by a single source, the relative angular distribution of neutrons from the source must be known. The sets of data obtained with several different sources can then be internormalized if the integrated neutron flux is known at one angle for each irradiation.

Three different neutron sources were used in this work: d-D sources at average deuteron energies of 2.00 and 4.98 Mev and a d-T source at 1.74 Mev deuteron energy. Both the 2.5 Mev and large Los Alamos electrostatic accelerators were used. For two of these sources (2.00 Mev d-D and 1.74 Mev d-T) the neutron flux was continuously monitored with a counter tele-

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† Work performed under the auspices of the U. S. Atomic Energy Commission. A preliminary report was given by J. Terrell and D. M. Holm, Phys. Rev. **95**, 650(A) (1954).

[1] A. H. Wapstra, Physica **21**, 385 (1955).

[2] Bartholomew, Hawkings, Merritt, and Yaffe, Can. J. Chem. **31**, 204 (1953).

[3] D. J. Hughes and J. A. Harvey, *Neutron Cross Sections*, Brookhaven National Laboratory Report BNL-325 (Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 1955).

[4] S. G. Forbes, Phys. Rev. **88**, 1309 (1952).

[5] E. B. Paul and R. L. Clarke, Can. J. Phys. **31**, 267 (1953).