Progress in studying the spectra of atoms and ions and the current level of knowledge about them

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This article treats briefly the fundamental stages of the study of the spectra of atoms and ions, which constitute the fundamental problem of atomic spectroscopy. Detailed data are presented on the current state of knowledge and the level of knowledge of the spectra of atoms and ions for all elements of the periodic system. The greatest level of knowledge of the spectra has been attained in the range from H to Mo. This involves the great progress in studying high-temperature plasmas, whereby spectra of 50-fold ionization have been obtained. One can see from analyzing the level of study of the spectra that 1063 spectra had been studied by December 1981, which amounts to 19.5% of the total number for the 104 elements. The presented data on the level of study of the spectra enable an investigator to select those necessary for plasma diagnostics, and also to plan a program of new spectroscopic studies.

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1. INTRODUCTION

The fundamental problem of atomic spectroscopy is to study the spectra of atoms and ions. On the basis of the rules established in the spectra, it has been possible to construct a model of the atom, to establish the energy levels for many atoms and ions, and to employ atomic spectroscopy for solving important scientific and practical problems. Atomic spectroscopy as the science studying the spectra of atoms and ions is a far from completed field.

The origin of the systematic study of the spectra of the chemical elements is considered to be 1859, when Kirchoff and Bunsen formulated the well-known law of the individuality of the line emission spectra for each element. This stimulated the study of atomic spectra and soon led to the discovery of 14 new elements in the Mendeleev table (Cs, Rb, Tl, In, He, Ga, Ge, Pr, Nd, Sm, Ho, Tm, Yb, and Lu). This law served as the starting point of the development of qualitative spectral analysis, and later also of quantitative analysis based on the dependence of the spectral lines on the concentration of the given element in the sample to be analyzed.

The first attempts to interpret atomic spectra were undertaken by Rydberg. In 1889 he established that the wave numbers of the spectral lines of certain chemical elements can be represented as differences between two numerical quantities, which he called spectral terms. On the basis of the differing structure of the spectral lines, he classified the terms into sharp, principal, and diffuse. Subsequently the initials of their English names began to be used as the designations of the electron shells of atoms and of terms. The physical interpretation of these symbols and a clear presentation of the atomic energy levels was given by Bohr in 1913, who created a theory of the atom based on spectroscopic data. He showed that atoms can exist in different atomic states having different energies. The spectral lines are the radiation that arises in the transition of an atom from one state to another, the radiation frequencies being proportional to the differences in energies of the atomic levels. The scientifically grounded spectroscopy of atoms and ions began to develop from this time, and included the classification of spectra and the establishment of energy levels.

2. THE STUDY OF SPECTRA FOLLOWING THE CREATION OF THE THEORY OF THE ATOM

It is interesting to examine how the study of the spectra of atoms and ions took place, starting in 1913, and what spectroscopic science has achieved at present. Our problem is facilitated by the publication in 1951 by the outstanding American scientist William Meggers of an article that collected the complete data on the study and classification of spectra of atoms and ions in the period from 1913 to 1951.[1] The article showed that 231 spectra of 69 chemical elements had been studied up to 1932. The energy levels obtained from analyzing the spectra were then published in the well-known book of Bacher and Goudsmit.[2] At that time, four elements had not been discovered (Tc, Pm, At, Fr) in the Mendeleev table from among the 92 elements from H to U. Since each chemical element can yield as many different spectra as it has electrons in the envelope of the neutral atom, the number of possible spectra then amounted to 4002. The level of study of spectra can be characterized by the ratio of all the studied spectra to the total number of spectra of the known elements. Thus, in 1932 the level of study of the spectra of atoms and ions had reached 231/4002, i.e., 5.8%.

By 1951, 273 new spectra had been studied. The total number of studied spectra had reached 504 for 84 elements. The energy levels of the atoms and ions were collected in a three-volume work (Moore[3]). At this time 98 chemical elements were known, including californium. However, the spectra of 14 elements yet remained unstudied (Pm, Ho, Er, Po, At, Fr, Ac, Pa, Np, Pu, Am, Cm, Bk, Cf). The number of possible spectra of the 98 elements amounted to 4851. Hence the level of study of spectra in 1951 was 504/4851, i.e., 10.4%.

In the following 30 years (from 1951 to December 1981), the scientists of many countries of the world have conducted a great effort to study the spectra of atoms and ions. This has been facilitated by the major advances in spectroscopic technique, which has involved problems that have arisen in which atomic spectroscopy has proved very useful. Among these we mention the spectral elemental and isotopic analysis of the products and materials used in atomic technology; the study of the complex spectra of the actinides and rare-earth elements and their hyperfine and isotopic structure; and the employment of spectroscopic diagnostics for determining the fundamental parameters of low- and high-temperature plasmas.

Consequently the situation has taken shape that new possibilities of development have arisen for atomic spectroscopy itself. New chemical elements have been discovered with the aid of nuclear reactors and weighable amounts of them have been obtained. Study has begun on the optical spectra of these elements, on classifying them, and establishing the energy levels of the neutral atoms and their first ions. Spectra of multiply charged ions have been obtained in installations for studying high-temperature plasmas.

Since 1967 many studies have been devoted to the spectra of highly ionized atoms. A substantial contribution has been made by Soviet spectroscopists. In the past 15 years, the Institute of Spectroscopy of the Academy of Sciences of the USSR under the direction of É. Ya. Kononov has studied 140 spectra of the ions of 26 elements in the range from aluminum to tin. The wavelengths of the spectral lines have been measured with high accuracy, they have been classified, and the energy levels established. A great effort has been made in the P. N. Lebedev Institute of Physics of the Academy of Sciences of the USSR under the direction of V. A. Boiko. Here the spectra of the hydrogen-like, helium-like, and lithium-like ions have been studied in the range of elements from sodium to sulfur, and also the spectra of ions of other elements. In all, about 50 spectra have been studied in the x-ray range from 20 to 2 Å.

To estimate the level of study of the spectra of atoms and ions in the past 30 years we have used the published journal articles collected in the bibliographic handbooks of the National Bureau of Standards (NBS) of the USA.[4-7] Moreover, we have taken account of the generalized data of selected tables on the atomic spectra of certain elements,[8] new books on the classified spectral lines of atoms and ions,[9-13] and on the energy levels of the rare-earth elements[14] and Grotrian diagrams,[15] as well as reference articles on these same subjects,[16-32] calculated data on the spectra and levels of hydrogen-like ions,[33,34] and collected volumes on ionization potentials.[35,36] We should add to this two review articles published in 1981. One of them treats the classification of spectra of highly ionized atoms in the past seven years.[37] It presents the results of extra-atmospheric studies of the emission spectra of the sun, together with spectra obtained by using different types of high-temperature plasma installations. The second article is devoted to the development of the spectroscopy of highly ionized atoms and its use for plasma diagnostics.[38]

In addition to these publications, our reference list presents studies[39-106] on the spectra of atoms and ions published since July 1979 that have not been included in the bibliographic handbooks of the NBS. These studies have enabled us to carry the treatment of the problem of the level of study down to December 1981. In a crude estimate, about 3000 original papers have been published in a 30-year period on the study of the spectra and energy levels of atoms and ions.

3. THE LEVEL OF STUDY OF SPECTRA AT PRESENT

Table I presents the situation in the level of study of the spectra of atoms and ions at present. The first column gives successively the symbols of the 104 chemical elements from hydrogen to kurchatovium. Each row in the table characterizes the degree of experimental study of all the studied spectra of the given elements, starting with the neutral atom and the sequential ions of increasingly multiple ionization. We have adopted the scale of Meggers[1] for the sake of comparability of the estimates of the level of study. The letter *A* denotes well studied spectra with a sufficiently complete system of energy levels and with an established coupling between the levels of differing multiplicities. The letter *B* denotes that the spectrum is rather well studied, and many levels of differing multiplicities have been found. The letter *C* characterizes a medium level of study of the spectrum: up to 20 levels have been found, but the coupling of the levels of differing multiplicity has not been established. The letter *D* indicates that up to 10

TABLE I. Level of study of spectra and energy levels in December 1981.

Z	Element	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52
1	H	A
2	He	A	A
3	Li	A	A	A
4	Be	A	A	A	A
5	B	A	A	A	A	A
6	C	A	A	A	A	B	A
7	N	A	A	A	A	A	B	A
8	O	A	A	A	A	A	A	B	A
9	F	A	A	A	A	A	A	B	B	A
10	Ne	A	A	B	A	A	A	B	B	B	A
11	Na	A	A	A	A	B	B	B	B	B	B	B
12	Mg	A	A	A	A	A	A	B	B	A	B	B	B
13	Al	A	A	A	A	A	A	A	B	B	B	B	B	B
14	Si	A	A	A	A	A	A	B	B	B	B	B	B	B	B
15	P	A	A	A	A	A	A	B	C	C	C	C	C	C	B	B
16	S	A	A	A	B	C	B	B	B	C	C	C	C	C	C	B	B
17	Cl	A	A	B	B	C	C	C	C	C	C	C	C	C	C	C	C	B
18	Ar	A	A	B	B	C	C	C	B	B	B	C	C	C	B	B	C	C	B
19	K	A	B	B	B	B	C	B	B	A	C	B	C	C	C	C	C	B	C	B
20	Ca	A	A	A	B	B	B	B	B	A	A	C	C	C	C	C	B	C	B	C	D
21	Sc	A	A	A	A	C	B	C	B	C	B	B	C	B	C	C	C	C	C	B	B	-
22	Ti	A	A	A	A	A	B	B	B	B	B	B	A	C	C	C	C	C	B	C	B	C	D
23	V	A	A	A	A	A	A	C	B	C	B	C	B	A	B	B	C	C	C	C	C	B	B	-
24	Cr	A	A	A	A	A	A	A	C	B	B	B	C	B	A	C	B	B	C	C	D	C	C	D	C
25	Mn	A	A	A	A	A	B	B	D	B	B	B	C	C	B	A	B	B	C	C	C	E	C	D	B	-
26	Fe	A	A	A	A	A	A	B	B	B	C	C	B	B	C	B	A	C	B	B	C	C	C	C	B	C	C
27	Co	A	A	A	C	A	B	B	B	C	C	C	C	D	D	C	B	B	C	C	C	C	C	C	C	C	C	-
28	Ni	A	A	A	A	A	A	A	B	C	C	B	C	C	C	B	C	C	A	B	B	C	C	E	C	B	B	B	-
29	Cu	A	A	A	A	B	A	e			B	C	C	C	D	E	C	D	C	B	C	B	C	C	C		D	D	C	C
30	Zn	A	A	B	B	D	D		E			D	D	C	D	D	D	C	D	C	B	C	C	C	C			C		D	-
31	Ga	A	A	B	B	B	B	B					E	E	E	E	E	E	E	E	C	B	C	D	D							-
32	Ge	A	A	c	c	B	B	B						E	E	E	E	E	E	E	E	C	B	C	C	D				E			-
33	As	A	A	C	C	B	B	C							E	E	E	E	E			E	C	B	C	C	D							-
34	Se	A	A	B	B	C	B	B	B							E	E		E	E			E	D	C	C	C	D				D			-
35	Br	A	B	C	C	C	d	C	C	B							E			E					D	C	C	C	D							-
36	Kr	A	A	B	C	C	C	D	B	C	C	D	D	D												E	E	D	D					E	E	D	-
37	Rb	A	A	A	C				D	D	C	d	e	e	e													E	D	E								-
38	Sr	A	A	A	A	C				D	A	b	d	C	e													E	E	D	E								-
39	Y	A	A	A	A	B	B	A	C	D	B	A	D	D	C	E													E	E	D	D	D							-
40	Zr	A	A	A	A	A	A	A	A	A	D	B	A	D	C	C														E	E	D	D	D							-
41	Nb	A	A	A	b	B	B	A	B	A	C	D	B	B	D	B	C	C													E	E	D	D	D							-
42	Mo	A	A	B	D	C	C	C	B	B	B	C	D	D	B	D	B	B	D	E	E	E	E	E	D	E	E	E	E	E	D	C	C	D	D	D					E	D	D
43	Tc	A	C
44	Ru	A	A	C					C	D	D					E	E	D	E															E	E
45	Rh	B	B	B						C	D	D						D	E																E	E
46	Pd	A	A	A							C	D	D					E	D	D	e																E
47	Ag	A	A	B	C							D	D					E	E	E	D	e									K							E	D								Li
48	Cd	A	A	A	B															E	E		e																	E
49	In	A	A	B	A	A	C														E	E		e																	E
50	Sn	A	A	c	C	A	B									Rb						E	D	E	D																	E
51	Sb	A	c	c	c	d	C	B															E	e		E
52	Te	A	B	c	C	C	D	C	C
53	I	A	A	e	d	D	D	D	D	B															E	E	E
54	Xe	A	A	A	C	E	D	D	C	D																E	E																		E	E	E	E
55	Cs	A	B	C						E	E	B
56	Ba	A	A	A	C						E	E																E	E																			Na
													Ag																		Cu
57	La	A	A	A	B	B						E	E																E	E
58	Ce	A	A	A	B	C	D						E	E
59	Pr	B	A	A	A	C								E	E
60	Nd	A	A	C	D	C	D								E	E																E	E
61	Pm	B	B	E	D
62	Sm	A	A	C	D												E	E																E	E	E
63	Eu	A	A	A	D													E	E
64	Gd	A	A	C	D														E	E																E	E	E	E	E
65	Tb	A	A	B	C															E	E
66	Dy	A	A	E	D	D															E	E																		D
67	Ho	A	C	B	C																	E
68	Er	A	A	C	D	D																																		E	E
69	Tm	A	A	B	D																																						E
70	Yb	A	A	B	D																																						E	E
71	Lu	A	A	A	B	C
72	Hf	A	A	B	B	B																																								D
73	Ta	A	A	D	B	B	B																																						E	E	D	E
74	W	A	A				B	B																					E																	D	E	D
75	Re	A	A					C	C																																								D
76	Os	A	B						C	D
77	Ir	A	C							D	E																					Ag
78	Pt	A	a								E	E																																								E
79	Au	A	A	B								E	E																																								E
80	Hg	A	A	B	D								E	E
81	Tl	A	A	B	D									E	E																																						Cu
82	Pb	A	A	A	B	b									E	E
83	Bi	A	B	C	C	d	b									E	E
84	Po	C	E
85	At	D																	Er
86	Rn	a	E						Au
87	Fr	D
88	Ra	a	a
89	Ac	C	D	D	E
90	Th	A	A	A	C	E
91	Pa	B	C	E
92	U	A	A	D	C	C	C
93	Np	B	D		D	E	E
94	Pu	A	B		D	E	E	E
95	Am	B	C	E	D
96	Cm	A	B
97	Bk	C	D		E	E
98	Cf	C	D		E
99	Es	D	D		E
100	Fm
101	Md
102	No
103	Lr
104	Ku

Notes. *A*—The spectrum is classified and a complete system of levels has been given. *B*—up to 30 levels of different multiplicities have been found. *C*—up to 20 levels have been found, and the coupling of different multiplicities has not been established. *D*—up to 10 levels have been found. *E*—one or several transitions have been established. Capital letters—level of study in January 1982; lower-case letters—in 1951.

levels are known. The letter E characterizes a preliminary level of study in which the wavelengths of lines have been measured, their assignment to a certain ionization stage has been established, and one or several transitions have been given. The lower-case letters a, b, c, d, and e denote the level of study of the spectra in 1951. This means that these spectra have not been studied in the following years.

We see from Table I that the spectra of the first 20 elements from hydrogen to calcium have been studied rather well in all the stages of ionization. Problems arise thereafter. The hydrogen-like spectra of Sc, V, Mn, Co, Ni, and the following elements except molybdenum have not been studied experimentally up to now. Calculated data exist for the spectra of these one-electron ions.[34] Starting with copper up to molybdenum, many spectra also have not been studied, or the level of study is low (E). After molybdenum the level of study of the spectra declines sharply. In this region only the spectra of the neutral atoms and some ions have been analyzed well. The studied spectra of the higher stages of ionization are grouped in the table in the form of isoelectronic sequences, which are marked by the slanted lines for Li I, Na I, K I, Cu I, Rb I, Ag I, Er I, and Au I. The studied spectra of multiply charged ions of adjacent isoelectronic sequences are arranged about these lines. The highest ionizations with multiplicity[45-52] have been obtained for the heavy elements in the region Hf–Au for the Ni-, Cu-, and Zn-like ions.

In Table II data are compiled that characterize the level of study of the spectra for seven groups of elements and for all elements as a whole. We see from the table that the level of study of the spectra declines with increasing atomic number Z of the elements owing to the insufficient level of study of the ions. This is explained by the experimental difficulties of exciting multiply charged ions and studying them, since the resonance lines of ions with a multiplicity of ionization above 10 and ionization potentials above 1 keV fall in the x-ray region. The high level of study of the first three groups of elements involves the expansion of the studies of high-temperature plasmas, which have facilitated the study of the spectra of the multiply charged ions with Z from 10 to 42. The level of study of the first three groups of elements has respectively reached 100, 94.9, and 55.5%. In the following groups this index falls to 19.6, 11.0, and 8.1%. For the radioactive elements

TABLE II. Level of study of spectra for different groups of elements.

Range of elements	Number of elements	Total spectra	During 1951-1981: Newly studied	During 1951-1981: Level of study improved	Total studied in Dec. 1981	Distribution by level of study: A, B	Distribution by level of study: C, D	Distribution by level of study: E	Number of unstudied spectra	Realtive level of study, %
H—Ar	18	171	30	77	171	138	33		none	100
K—Zn	12	294	137	117	279	144	130	5	15	94.9
Ga—Mo	12	438	161	43	243	82	99	62	195	55.5
Tc—Ba	14	693	70	22	136	41	51	44	557	19.6
La—Lu	15	960	78	23	106	42	28	36	854	11.0
Hf—Bi	12	930	42	20	75	38	17	20	855	8.1
Po—Ku	21	1974	44	5	53	12	26	15	1921	1.3
All spectra	104	5460	562	307	1063	497	384	182	4397	19.5

TABLE III. Level of study in different periods.

Year	Total level of study of spectra	Studied in the given period	Number of studied spectra per year	Year	Total level of study of spectra	Studied in the given period	Number of studied spectra per year
1913	0	0	0	1951	504	59	11.8
1922	38	38	4.2	1959	511	7	0.9
1932	231	193	19.3	1969	648	137	13.7
1939	400	169	24.1	1981	1063	415	34.6
1946	445	45	6.4				

(Po–Ku), the level of study declines to 1.3%. In this region only 53 spectra out of 1974 spectra have been studied. The last row of Table II shows that all the chemical elements known at present possess 5460 spectra. Of these, 1063 spectra have been studied. Hence the level of study of the spectra for all elements is found to be 19.5%. Only one-half of these spectra has been studied well (A and B)—47%, while the rest require further studies. And a fifth of them falls in group E—17%. That is, their study is just beginning.

Our article on examining the level of study of the spectra of atoms and ions was mainly prepared up to mid-1981. The article of Cowan[38] became known in December. It turned out that the tables of the level of study almost fully coincide. They differ only in estimates of the level of study of a number of spectra, which apparently involves a certain difference in the established criteria, and perhaps subjective estimates. According to Ref. 38, 1019 spectra had been studied in March 1981. The present article covers the published literature up to December 1981 inclusive.

4. CONCLUSION

Upon using the data of Ref. 38 and the level of study of 1063 spectra established in December 1981, we can trace in greater detail the development of studies of the spectra, beginning in 1913 up to the present. Table III presents the change in the level of study of the spectra with time. The first column indicates the year of the estimate of the level of study of the spectra, the second column gives the overall level of study in this year, and the third and fourth columns give the number of studied spectra and the mean level of study per year over the given period.

Undoubtedly the first increase in the study of spectra (1922–1939) was caused by the development of the Bohr theory for complex atoms, and the second maximum involves the advances in studying spectra of multiply charged ions (1969–1981). The minimum pertains to the war and postwar years. A certain growth in the period 1946–1951 involves the study of the spectra of the newly discovered actinides and other radioactive elements.

We note in conclusion that much attention is being paid at present to studying the spectra of atoms and ions, and considerable advances have been attained in the past decade. Up to 1982 the level of study of the spectra for all elements amounted to 19.5% as compared with 10.4% in 1951. If we take into account the theoretical calculations for hydrogen-like atoms,[34] the spectra have been studied for all stages of ionization for the first 28 elements (H–Ni). The level of study of the subsequent elements from Cu to Mo still remains insufficient, and has reached 60.8%. Here 195 spectra out of 497 have not been studied, and for 68 spectra only several classified lines each have been established. Undoubtedly these spectra will be of important value in studies of high-temperature plasmas. Therefore in the very near future the efforts of spectroscopists studying the spectra of ions will be directed toward solving these problems.

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