7c. Energy-level Diagrams of Atoms

A number of energy-level diagrams are represented in Figs. 7c-1 through 7c-15. An attempt has been made to select typical cases which show characteristic features derived from optical spectra. The following comments may be helpful.

In almost all cases the energy levels have been arranged according to the Russell-Saunders scheme, also called L, S coupling. This means that each level is characterized by the total orbital angular momentum L, the resultant spin S or rather the multiplicity $2S + 1$ [1 for singlets ($S = 0$), 2 for doublets ($S = \frac{1}{2}$), 3 for triplets ($S = 1$), etc.], and its total angular momentum quantum number J. The scale of the figures usually does not permit showing the individual multiplet components. However, the total width is indicated unless it is no greater than the thickness of the line.

Even levels are shown by entire lines or blocks, odd levels by broken ones. When an entire column has the same parity as in the simple spectra, the odd parity is indicated by the term symbol at the bottom of the column in the usual way, e.g., $^3F^0$.

The horizontal line across the whole width of the diagram is at the first ionization potential. This is indicated by the term symbol for the ground state of the ion. In some cases higher ionization potentials are also indicated.

The electron configuration is given by symbols explained with each individual diagram.

Transitions which correspond to spectrum lines are left out in order to avoid confusion except for the important lowest transitions which often give rise to the strongest lines. The resonance line R is the lowest transition to the ground state allowed by the selection rules of L, S coupling, which are change of parity, no change in multiplicity ($\Delta S = 0$), and $\Delta J = 0 \pm 1$. The subresonance line r is a line from a lower level than that responsible for the resonance line; it obeys the same selection rules except $\Delta S = 0$. It is usually very weak for the lighter atoms but may be quite strong for the heavier elements (e.g., 2,537 of Hg).

The spectra represented in the figures are given in Table 7c-1.

TABLE 7c-1. SPECTRA REPRESENTED BY FIGS. 7c-1 THROUGH 7c-15

Z	Element	Figure
2	He I	7c-1
6	C I	7c-2
7	N I	7c-3
8	O I	7c-4
11	Na I	7c-5
13	Al I	7c-6
17	Cl I	7c-7
18	A I	7c-8
20	Ca I	7c-9
25	Mn I	7c-10
26	Fe II	7c-11
	Fe I	7c-12
29	Cu I	7c-13
80	Hg I	7c-14
57–70	Ce IV-Yb IV	7c-15

Further diagrams of simple spectra are found in Grotrian.[1]

[1] W. Grotrian, "Graphische Darstellung der Spektren von Atomen und Ionen mit ein, zwei, und drei Valenzelektronen," vol. 1, 245 pp.; vol. 2, 268 pp.; Springer-Verlag OHG, Berlin, 1928.

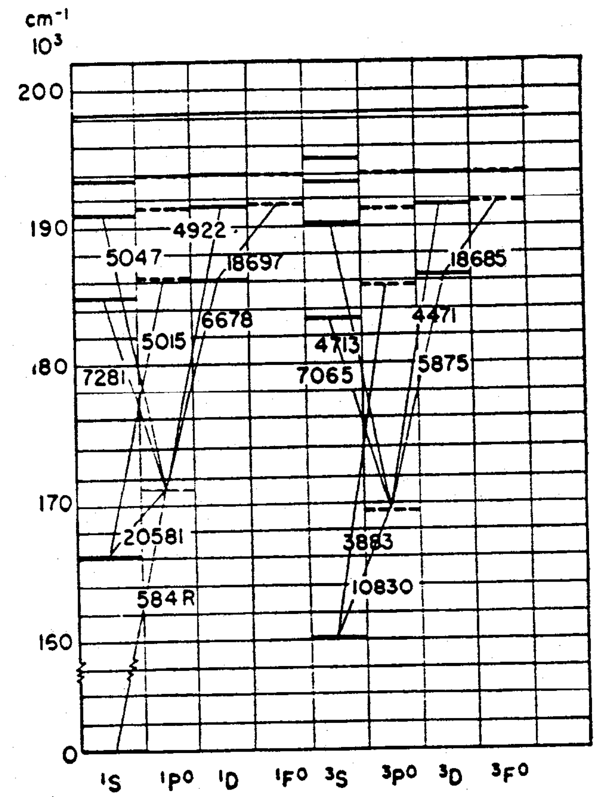

FIG. 7c-1. Energy-level diagram of He I—simplest atom with two valence electrons. The wavelengths of the principal lines are indicated.

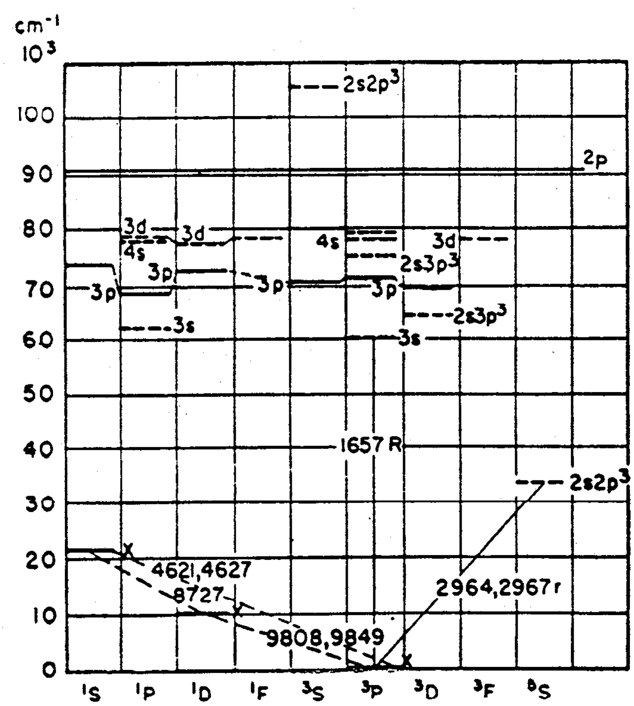

FIG. 7c-2. Energy-level diagram of C I—four valence electrons, lowest state $2s^22p^2$. Most excited states are $2s^22p \cdot nx$. The orbit nx of the last electron only is indicated in the figure except where one of the $2s$ electrons is excited, as, for instance, $2s2p^3$. The important forbidden lines are indicated.

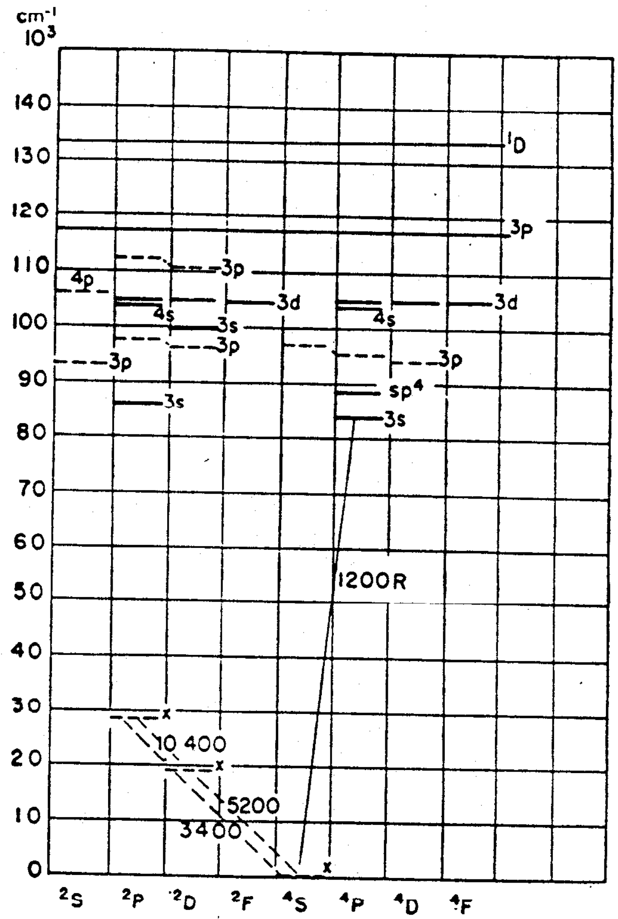

FIG. 7c-3. Energy-level diagram of N I—five valence electrons, normal state $2s^22p^3$. Excited states are $2s^22p^2 \cdot nx$, nx being indicated in the figure. When the $2s$ electron is excited, the full configuration is given, e.g., $2s2p^4$. The important forbidden lines are indicated.

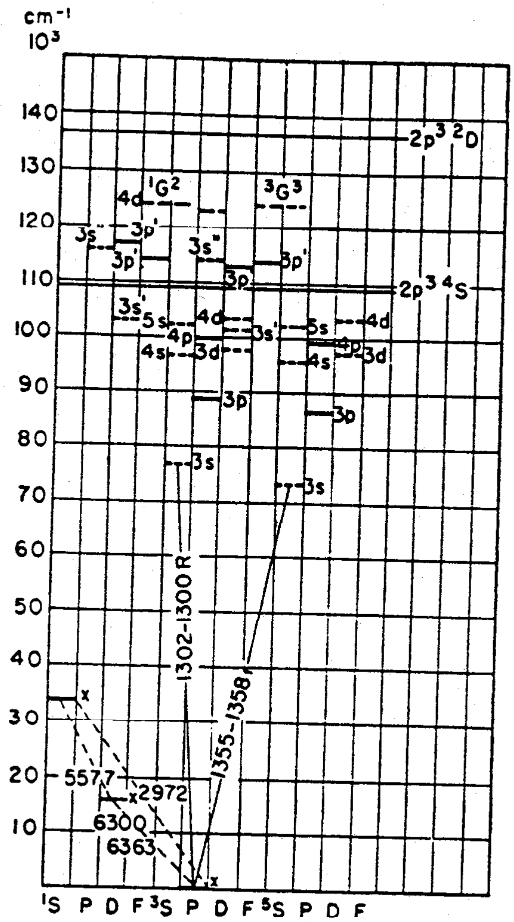

FIG. 7c-4. Energy-level diagram of O I—six valence electrons. Normal state is $2s^22p^4$; excited states are $2s^22p^3 \cdot nx$, nx being indicated in the figure. The important forbidden lines are indicated.

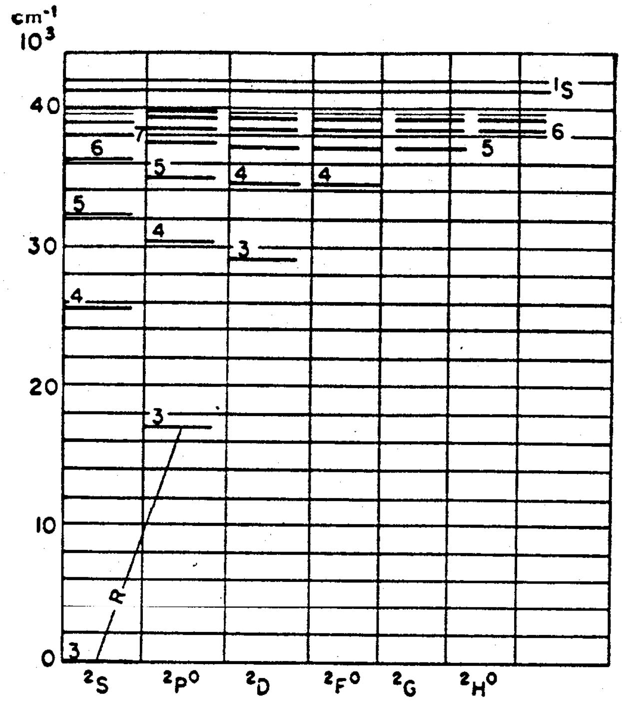

FIG. 7c-5. Energy-level diagram of Na I. Simple diagram typical for elements with one valence electron. The other alkalies have essentially the same scheme.

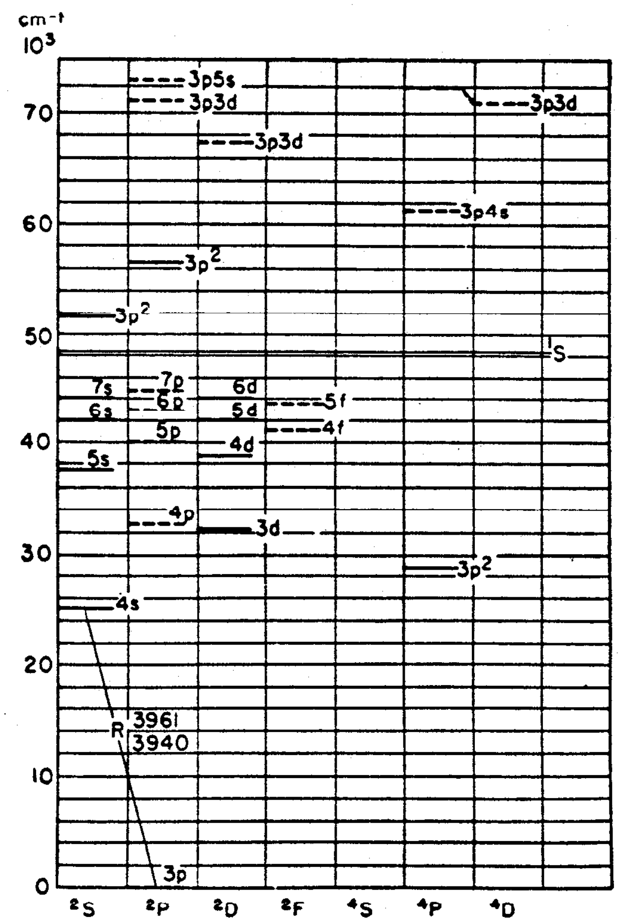

FIG. 7c-6. Energy-level diagram of Al I—three valence electrons. Normal state is $3s^2 3p$, excited states $3s^2 \cdot nx$ (nx is indicated) or $3s3pnx'$ (nx' is indicated with primed letters). The primed levels converge to a higher ionization limit.

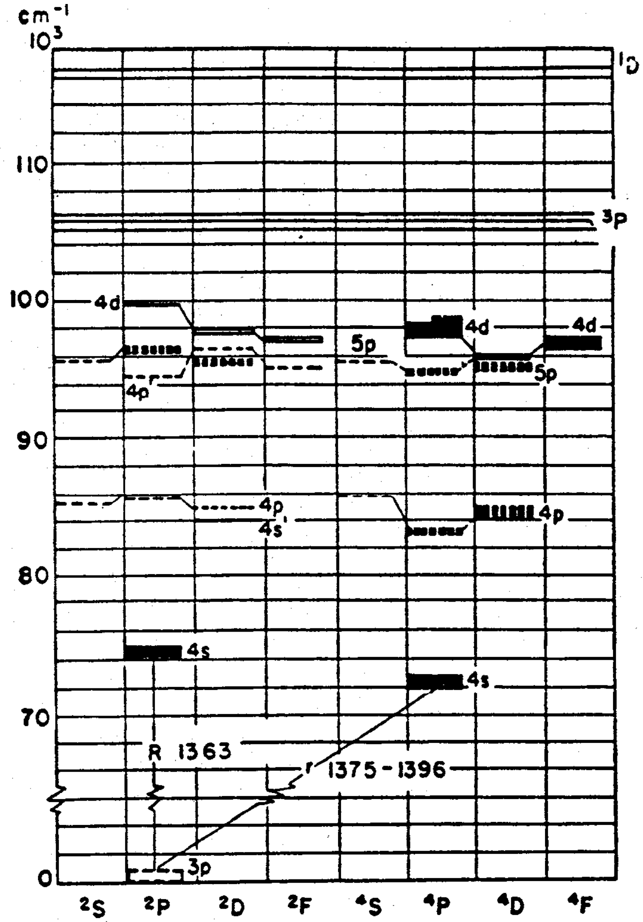

FIG. 7c-7. Energy-level diagram of Cl I—seven valence electrons. Ground state is $3s^23p^5$, excited states $3s^23p^4nx$, nx being indicated in the figure.

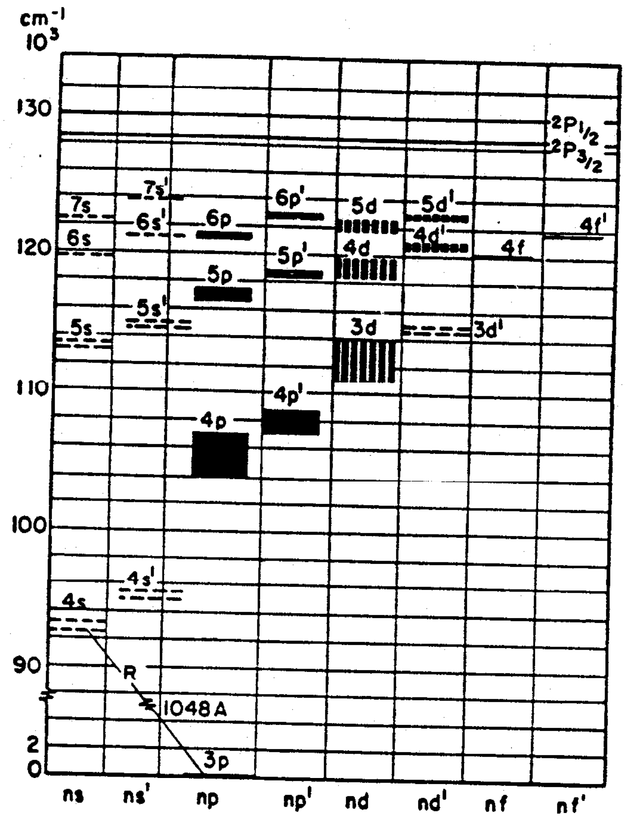

FIG. 7c-8. Energy-level diagram of A I—typical for the rare gases except helium. Levels $3s^23p^5 \cdot nx$ with nx indicated. L,S coupling is not appropriate here and therefore symbols like ^3P, etc., have no meaning. The primed levels converge to the higher ionization potential. See also Table 7e-3.

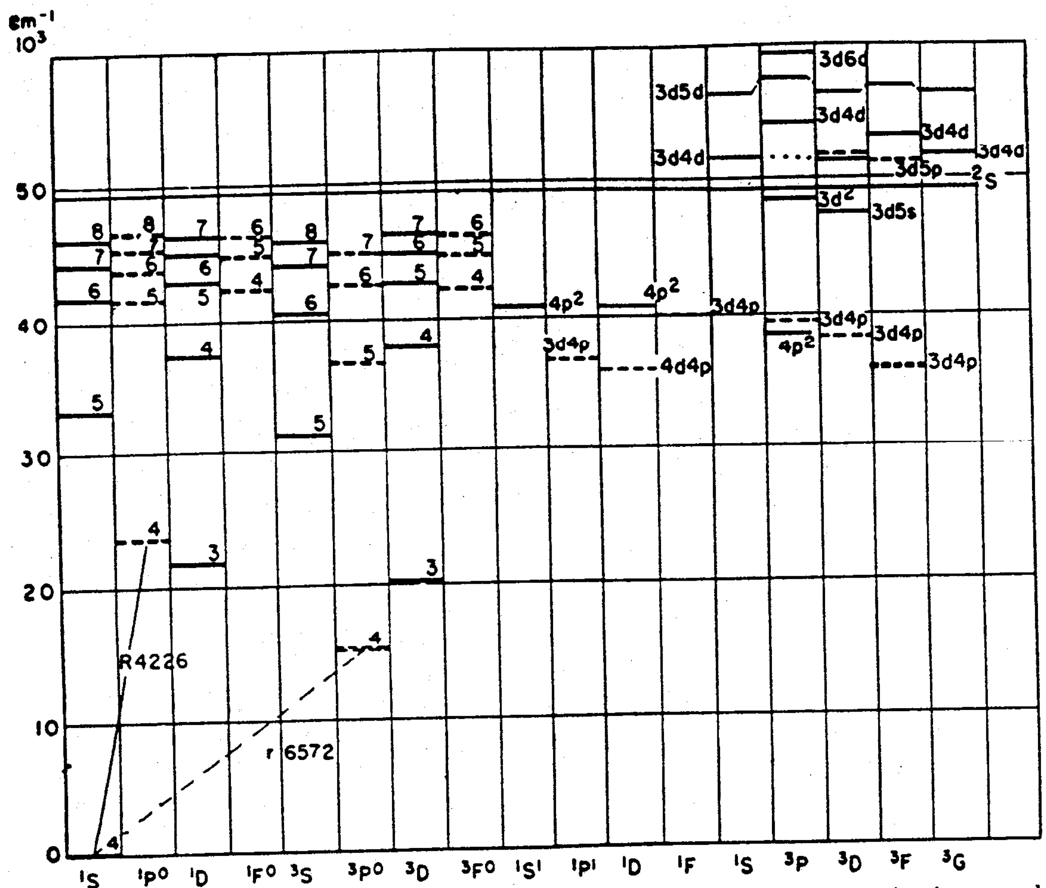

FIG. 7c-9. Energy-level diagram of Ca I. Characteristic for the elements in the second column of the periodic system. Ground state $4s^2$ and regular excited states $4s\ nx$ are indicated only by the value of n in the appropriate column. Levels with both electrons excited are given at the right.

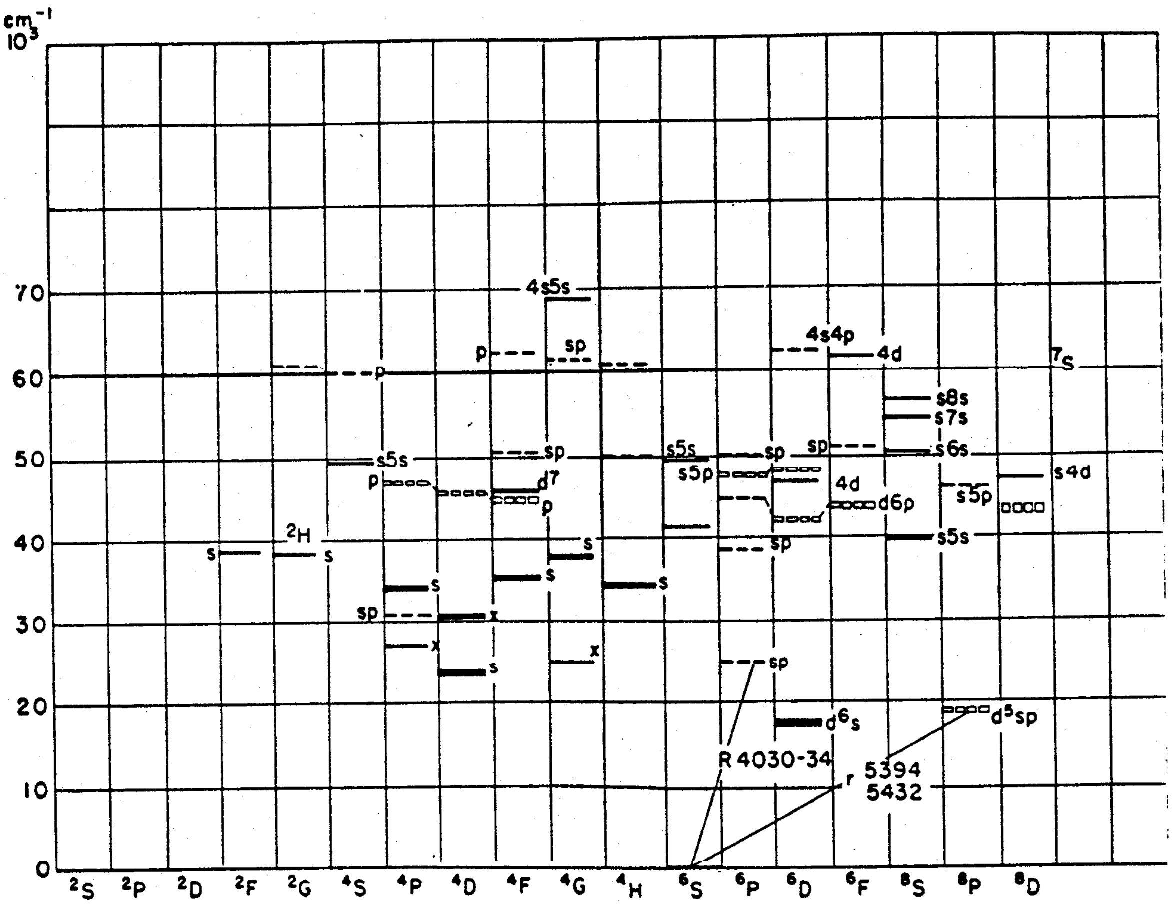

FIG. 7c-10. Energy-level diagram of Mn I. A typical element of the transition group. Seven valence electrons. Ground state $3d^54s^2$. This produces 16 multiplet levels of which only four (^6S, ^4P, ^4D, ^4G) are known. They are marked by an x. The other low states are $3d^64s$ (s), $3d^64p$ (p), $3d^54s4p$ (sp), $3d^54p^2$ (p^2), $3d^7$ (d^7). The symbol between parentheses indicates how the level is marked in the figure. If higher than $3d$, $4s$, $4p$, electrons are involved, the value of n is marked, e.g., $3d^54s5p$ ($s5p$) or $3d^54s4d$ ($s4d$). In general, the number of $3d$ electrons is left out in the figure (except for $3d^7$). Compare Mn I with Fe II, which has the same number of electrons (Fig. 7c-11).

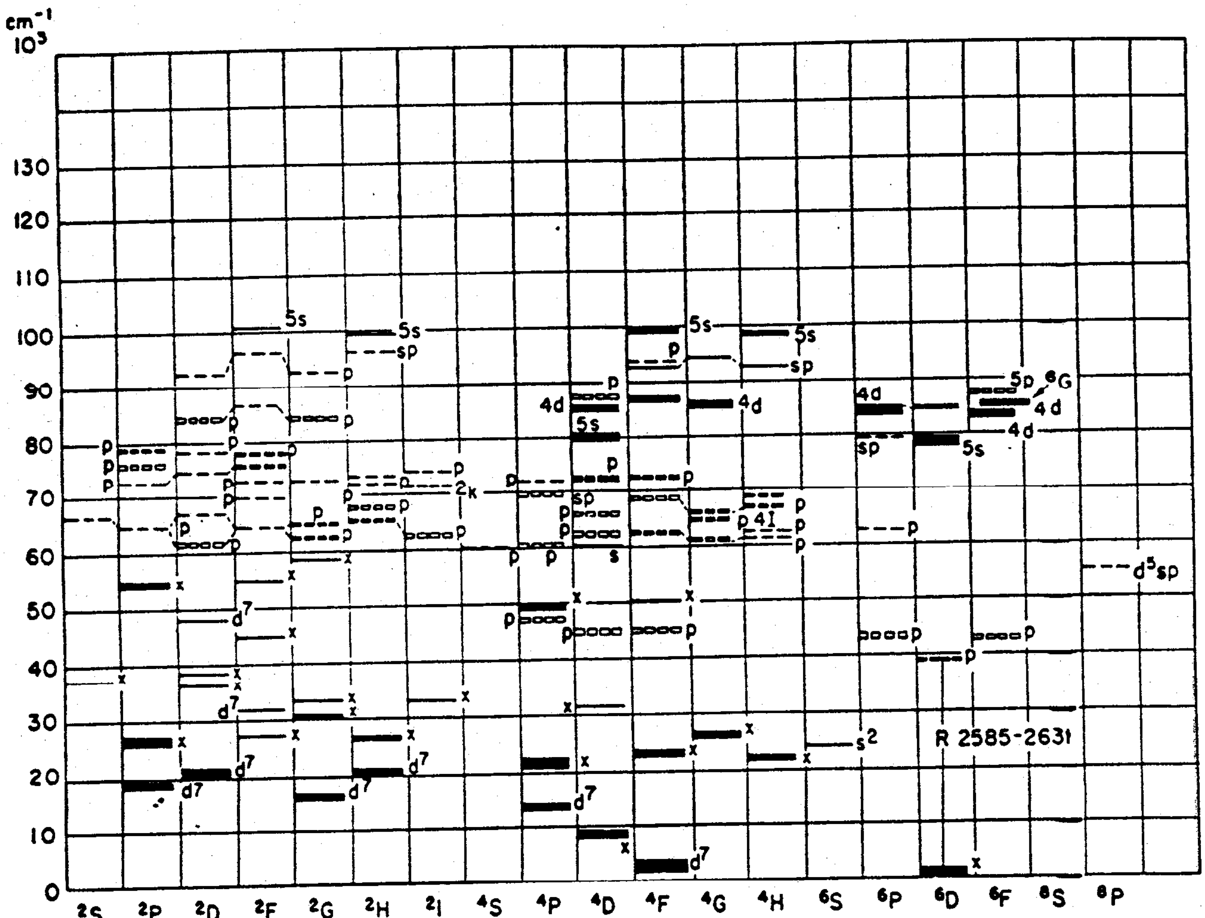

FIG. 7c-11. Energy-level diagram of Fe II. Fe II has the same number of electrons as Mn I and therefore the same type of levels. The relative position of the levels is, however, greatly changed by the increase in the nuclear charge. In general, there is a tendency for levels containing 3*d* electrons to be lower than those with 4*s* or 4*p* electrons. The ground state is $3d^64s$. There are 24 multiplet levels of this configuration, of which 23 are known (marked with *x*). The excited levels are marked as for Mn I.

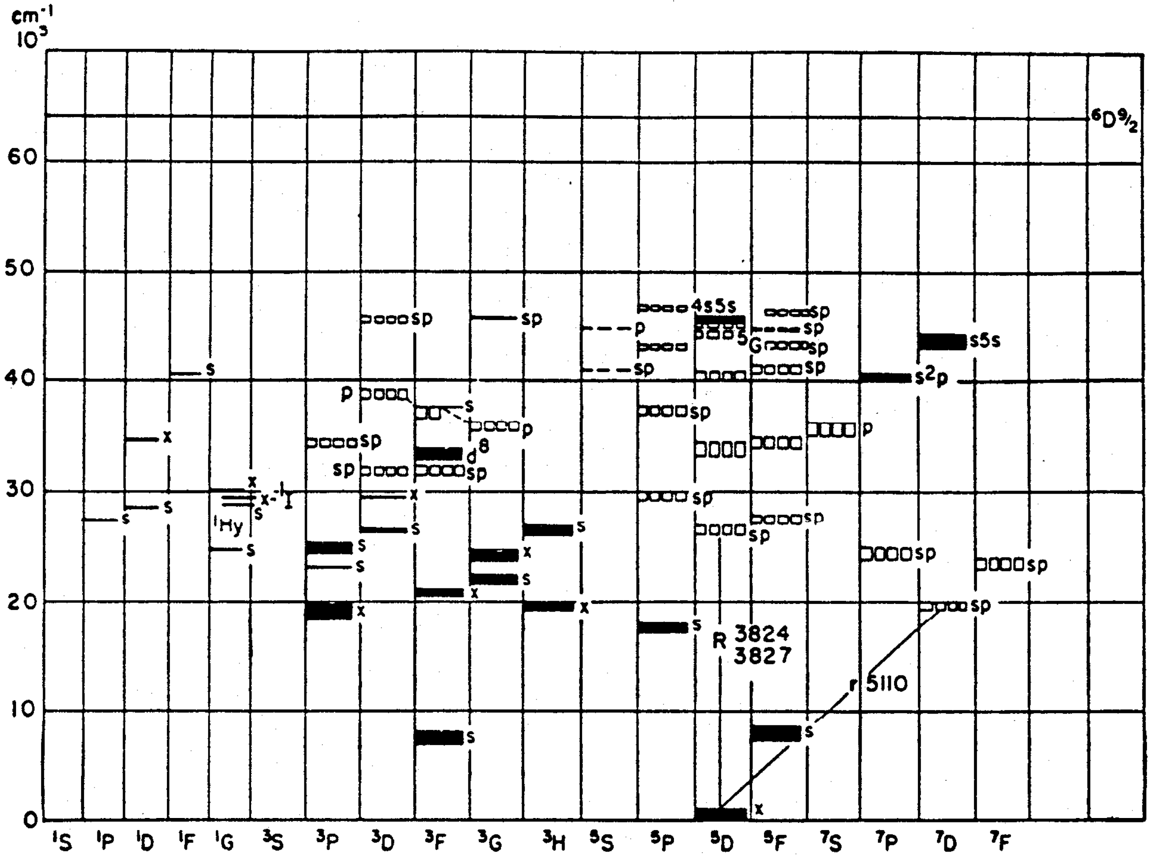

FIG. 7c-12. Energy-level diagram of Fe I. The spectrum of Fe I is one of the best studied and is of particular importance because of the use of iron lines for wavelength standards and other applications (see Table 7e-6). Eight valence electrons, ground-state configuration $3d^64s^2$, which gives 16 multiplet levels, of which 9 are known (marked x in the figure). Other configurations leading to low-lying levels are $3d^74s$ (s), $3d^64s4p$ (sp), $3d^8$ (d^8), $3d^74p$ (p), $3d^54s^24p$ (s^2p). If n values higher than for $3d$, $4s$, $4p$ are involved, they are indicated as, e.g., $3d^64s5s$ ($s5s$).

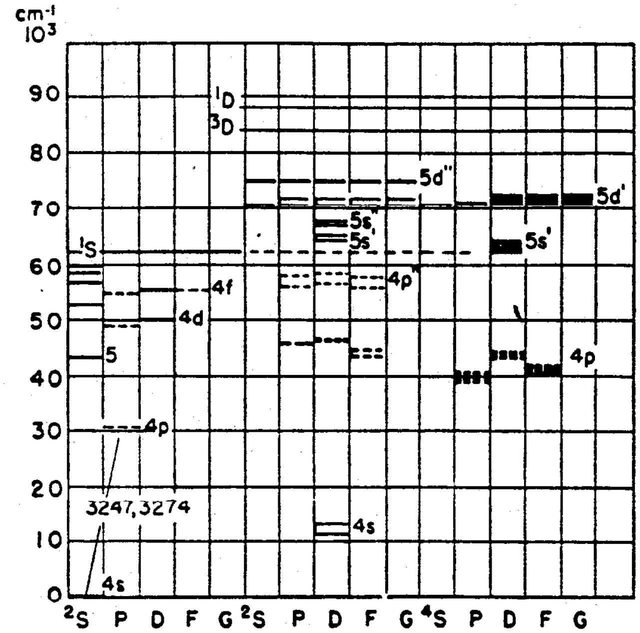

FIG. 7c-13. Energy-level diagram of Cu I. The arrangement of the outer electrons is $3d^{10}4s^2S$ in the ground state. If the 4s electron is excited, the levels are very similar to those of an alkali as shown, e.g., in Fig. 7c-5. These regular levels are indicated at the left. If one of the 3d electrons is excited, levels of more complicated structure arise as indicated at the right.

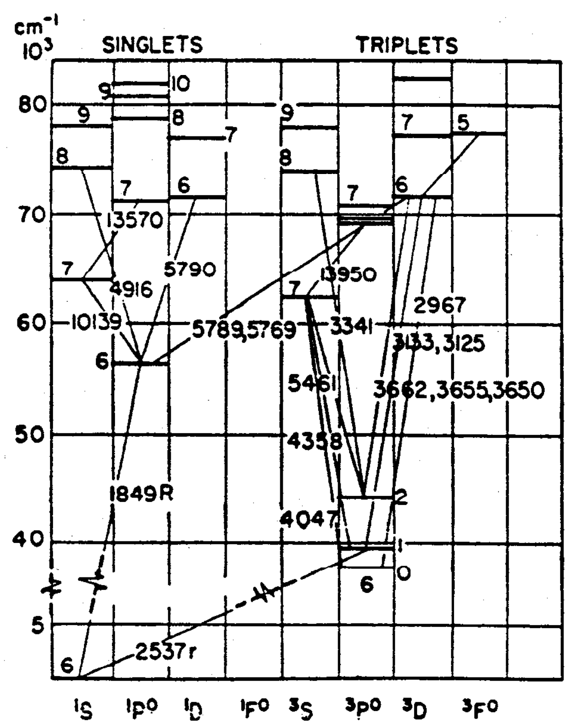

FIG. 7c-14. Energy-level diagram of Hg I. This is the diagram of a typical two-electron spectrum with singlets and triplets. Because of the wide use of the mercury spectrum in many applications, the wavelengths of many transitions are indicated. Single triplet transitions are relatively strong. See also Table 7e-7 and Figs. 7e-5 and 7e-6.

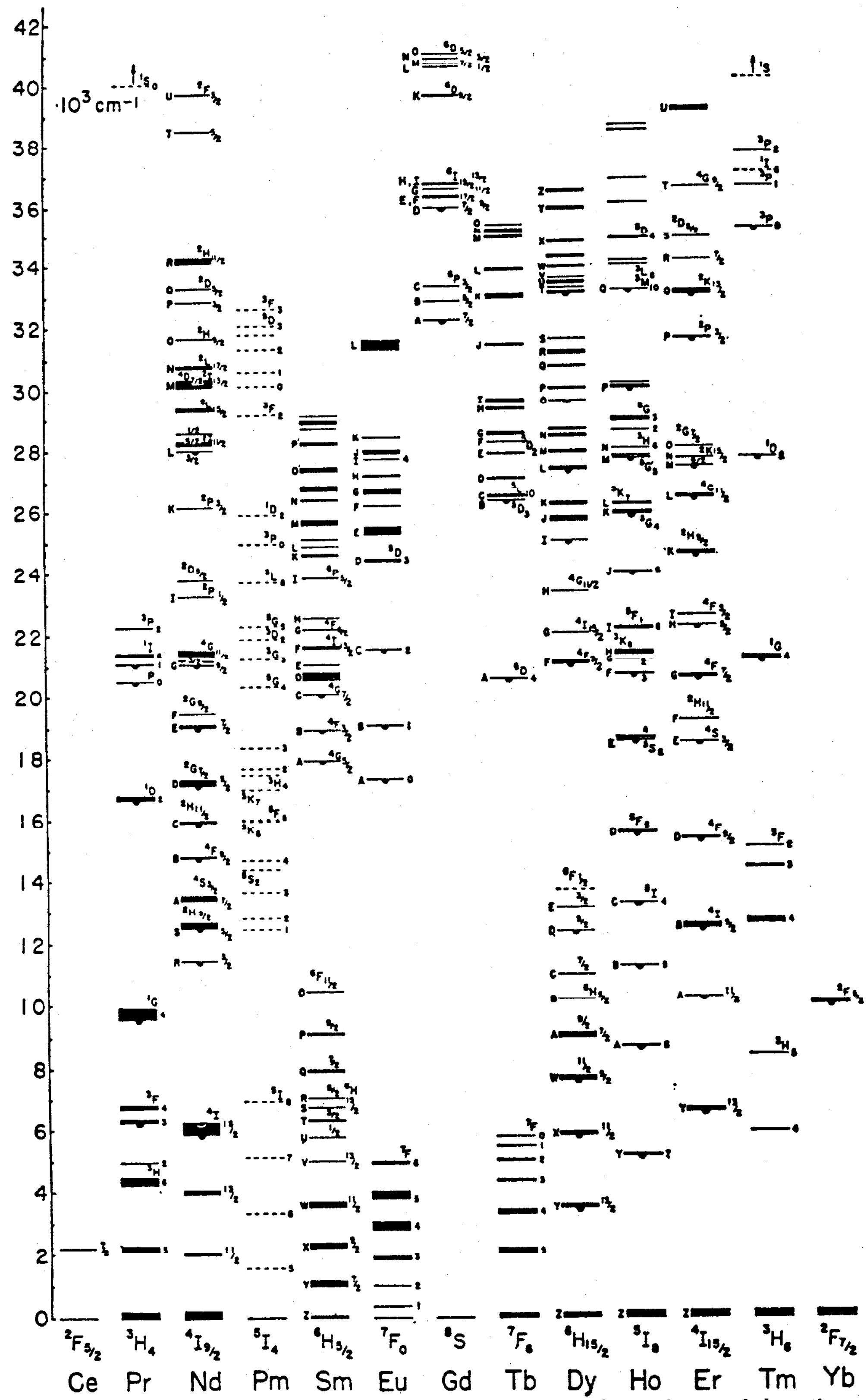

Fig. 7c-15. Lowest energy levels of the three-valent ions as determined from the crystal absorption and fluorescence spectra. (In most cases the data are for anhydrous chloride.) The thickness of the levels indicates the amount of splitting of the free ion level in the crystal field. The ground state is indicated on the bottom; the excited states are designated by empirical letters *A*, *B*, *C*, etc., or by the equivalent *LS* coupling symbols like $^5D_2$. The *J* values are given at the sides. The data for Pm are tentative. The scheme is complete to about 25,000 cm.$^{-1}$ A semicircle under a level shows that it is the upper state of fluorescence transitions. (*Source of data, The Johns Hopkins University.*)