

## optical spectra

The outer electrons of an atom determine the chemical and optical properties of their atoms. The electrons in the closed inner orbits do not take part in the emission of spectral lines.

### spectral terms:

Atoms are divided into two main categories, viz one electron system and many-electron system.

- (i) The alkali metals (such as lithium, sodium and potassium) have a single valence electron outside completely filled subshell.

The valence electrons in the alkali metals therefore behaves much like the orbiting electron in the hydrogen atom. Hence the alkali metals have a hydrogen like spectra. Their spectrum is also referred to as the one-electron spectra.

- (ii) In the many-electron system, the atoms have more than one valence or optical electron outside completely filled subshells. Hence they become effective in fixing the spectral properties.

For example,

The alkaline earths belonging to the two-electron system have spectra which are similar among themselves.

### Spectral notations:

The states of the atom, in which the values of its  $L$  vector are 0, 1, 2, 3, 4, 5 are represented by the capital letters, S, P, D, F, G, H etc. respectively. The value of the total angular momentum of the atom  $J$  is written as a subscript at the lower right of the letter representing the particular  $L$  value of the atomic state. The multiplicity of the total spin ( $S$ ) is written as a superscript at the upper left of the letter. If  $S$  is the total spin the multiplicity is equal to  $2S + 1$ .

### Example:

- (i) A state with  $L = 1$ ,  $S = 1/2$  and  $J = 3/2$  is written as  $^2P_{3/2}$  and read as doublet-P three halves.
- (ii) A state with  $L = 2$ ,  $S = 1$  and  $J = 2$  would be written as  $^3D_2$  and read as triplet-D two.
- (iii) The spectral terms corresponding to  $L = 1$  and  $S = 1/2$  can be written as  $^2P_{1/2}$  and  $^2P_{3/2}$ .  
[Since  $L = 1$ , the capital letter which represent  $L$  is P, the multiplicity of the state  $= (2 \times \frac{1}{2} + 1 = 2)$  This is put as superscript;  $J = L \pm S$ .

$$\therefore J = L + S \quad + \quad J = L - S$$

$$= 1 + 1/2$$

$$3/2$$

$$= 1 - 1/2$$

$$1/2$$

$$\therefore ^2P_{3/2} \quad + \quad ^2P_{1/2}$$

## Intensity Rules

Whether an allowed transition is weak or strong is determined by what is known as intensity rules.

They are

- (i) The transitions for which  $L$  and  $J$  change in the same way (i.e.  $\Delta J = \Delta L$ ) are strong. For other changes in  $L$  and  $J$  ( $\Delta L \neq \Delta J$ ) we get weak transitions.
- (ii) Transitions for which  $L$  and  $J$  increase (i.e.  $L \rightarrow L+1$  and  $J \rightarrow J+1$ ) are less intense than those for which  $L$  and  $J$  decrease (i.e.  $L \rightarrow L-1$  and  $J \rightarrow J-1$ ).
- (iii) Transitions for which changes in  $L$  and  $J$  are opposite (i.e.  $\Delta L = -\Delta J$ ) are forbidden. Symbolically, these intensity rules are written as

$$\Delta L = -1 \quad \Delta J = -1 \quad \text{strongest}$$

$$\Delta L = -1 \quad \Delta J = 0 \quad \text{less intense}$$

$$\Delta L = +1 \quad \Delta J = +1 \quad \text{weak}$$

$$\Delta L = +1 \quad \Delta J = 0 \quad \text{very weak}$$

$$\Delta L = -1, \quad \Delta J = +1 \quad \left. \vphantom{\begin{matrix} \Delta L = -1 \\ \Delta L = +1 \end{matrix}} \right\} \text{forbidden.}$$

$$\Delta L = +1, \quad \Delta J = -1 \quad \left. \vphantom{\begin{matrix} \Delta L = -1 \\ \Delta L = +1 \end{matrix}} \right\} \text{forbidden.}$$

## The interval rule:

Lande discovered a rule regarding the interval in frequency between the different levels constituting a multiplet. It states that the frequency interval between two levels with total angular momentum ( $J+1$ ) and  $J$  respectively is proportional to  $(J+1)$ .

## Selection rules

An electron cannot jump from one energy level to all other energy levels. A transition of an electron between two levels is possible only if certain rules called selection rules are satisfied. For the vector atom model, three selection rules have been devised.

- (i) The selection rule for  $L$  is  $\Delta L = \pm 1$  i.e. only those lines are observed for which the value of  $L$  changes by  $\pm 1$ .  
For example.

$L$  can change from 0 to 1 ( $\Delta L = +1$ ) or from 1 to 0 ( $\Delta L = -1$ ).  $L$  cannot change from 0 to 2 ( $\Delta L = +2$ ) or from 2 to 0 ( $\Delta L = -2$ ). In symbols the transition is possible between s and p levels ( $\Delta L = \pm 1$ ) but not possible between s and d levels ( $\Delta L = \pm 2$ ).

- (ii) selection rule for  $J$ :  $J = \Delta J = \pm 1$  or 0  
But  $0 \rightarrow 0$  is excluded.

- (iii) selection rule for  $S$ : is given by  
 $\Delta S = 0$ .

# Fine structure of the sodium line.

## D-line.

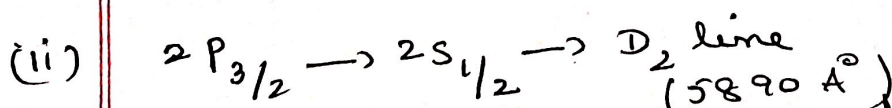
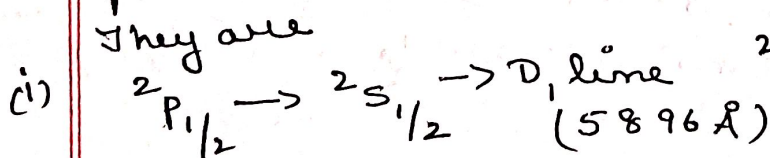
Ten out of the eleven electrons of the normal sodium atom are interlocked in closed shells. They contribute nothing to the angular momentum of the atom. We have to consider only the ~~at~~ states of eleventh optical electron in discussing the spectrum of neutral sodium.

D-line belongs to principal series. Lines of the principal series are due to transitions from P state to the S state.

For the upper P state,  $L=1$ ,  $J=L \pm S = 3/2$  or  $1/2$ . Hence the two possible terms are  $^2P_{3/2}$  and  $^2P_{1/2}$ . For the lower S state  $L=0$ ,  $J=1/2$  so that only one term  $^2S_{1/2}$  is possible.

Figure 1 shows two possible transition between the two terms of the P state and the single term of the S state.

They are



Now applying selection rules  $\Delta L = \pm 1$  and  $\Delta J = \pm 1$  or  $0$  (excluding  $0 \rightarrow 0$ ), both these transitions are allowed.

