

## Electronic Spectroscopy

- Here the quantum states  $\Psi_i$  and  $\Psi_f$  are *electronic* states of the system. Again, we need

$$\int \Psi_i O \Psi_f d\tau \neq 0,$$

where  $O$  is the appropriate transition operator.

- Once again, the most important case is electric dipole radiation, with the same general selection rules as before.
- For a spin-free Hamiltonian, there are no *intercombination bands* — allowed transitions connect terms of the same spin only.
- First example of spectroscopy on atoms.



## Electronic Transitions in Atoms

- For atoms the electric dipole vector transforms as  $P^{\circ}$ .
- This leads immediately to the *Laporte* rule that allowed transitions occur only between even and odd parity states.
- From the Clebsch-Gordan series we know that  $\Gamma(L = 1) \otimes \Gamma(L = L')$  gives states with  $L = L' - 1, L', L' + 1$  (except for  $L' = 0$ ), so we expect dipole transitions in which  $\Delta L = 0, \pm 1$ .
- Can particularize to transitions between  $J$  levels.
- Sidebar: B atom, orbital model.



## Electronic Transitions in Diatomics

- The analysis is similar to atoms, except that the “angular momentum” is now the projection on the internuclear axis.
- The symmetry species of the dipole vector is  $\Sigma^+$ ,  $\Pi$ , so we expect transitions in which the angular momentum projection changes by 0 or  $\pm 1$ .
- There are some restrictions, such as  $\Sigma^+$  and  $\Sigma^-$  do not connect. And in homonuclear diatomics the analog of the Laporte rule applies.
- Sidebar:  $O_2$ .



## Polyatomic Molecules

- Use selection rules as usual.
- For polyatomic molecules vibrations of different symmetry species are possible. Since the Born-Oppenheimer approximation is not perfect, vibration often plays a role in molecules.
- Sidebar:  $\pi$ -electron spectra in  $C_6H_6$ , vibrations, intercombination bands.



## Fluorescence, Phosphorescence

- The possibility exists of populating excited electronic levels which are long-lived (that is, transitions back to the ground state are formally forbidden).
- The commonest situation is populating the lowest excited triplet state in a system with a singlet ground state.
- This requires double groups for a proper symmetry analysis, but can often be understood without this.
- Sidebar: fluorescence in octahedral  $\text{Cr}^{3+}$ .

