Electronic Spectroscopy of molecules

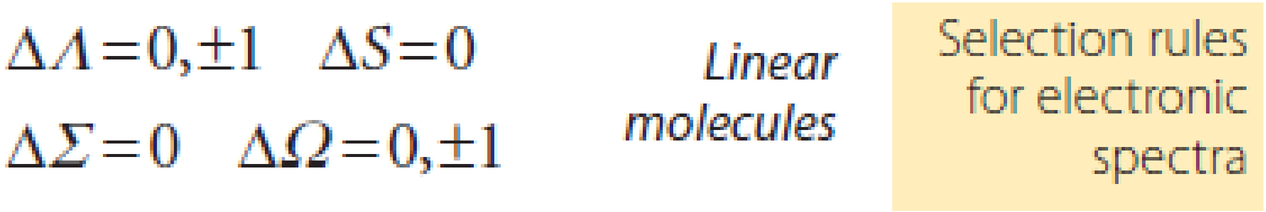
Part III: Electronic transitions

B.Sc. (H) Chemistry

Dr Anil Kumar Singh
Department of Chemistry
Mahatma Gandhi Central University

Selection Rule

- A number of selection rules govern which transitions can be observed in the electronic spectrum of a molecule. The selection rules concerned with changes in angular momentum are:



$$\Delta\Lambda = 0, \pm 1 \quad \Delta S = 0$$

$$\Delta\Sigma = 0 \quad \Delta\Omega = 0, \pm 1$$

Linear molecules

Selection rules for electronic spectra

  - The latter Σ *is* the component of the electron spin on that axis, where $\Sigma = S, S-1, S-2, \ldots, -S$.

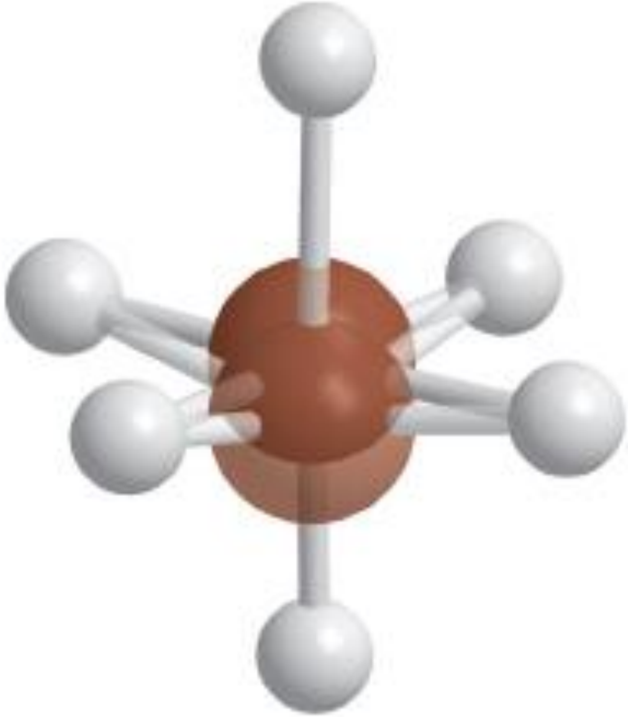
- There are two selection rules concerned with changes in symmetry.

  First, as we show in the following *Justification*,

  For Σ terms, only $\Sigma^+ \leftrightarrow \Sigma^+$ and $\Sigma^- \leftrightarrow \Sigma^-$ are allowed.

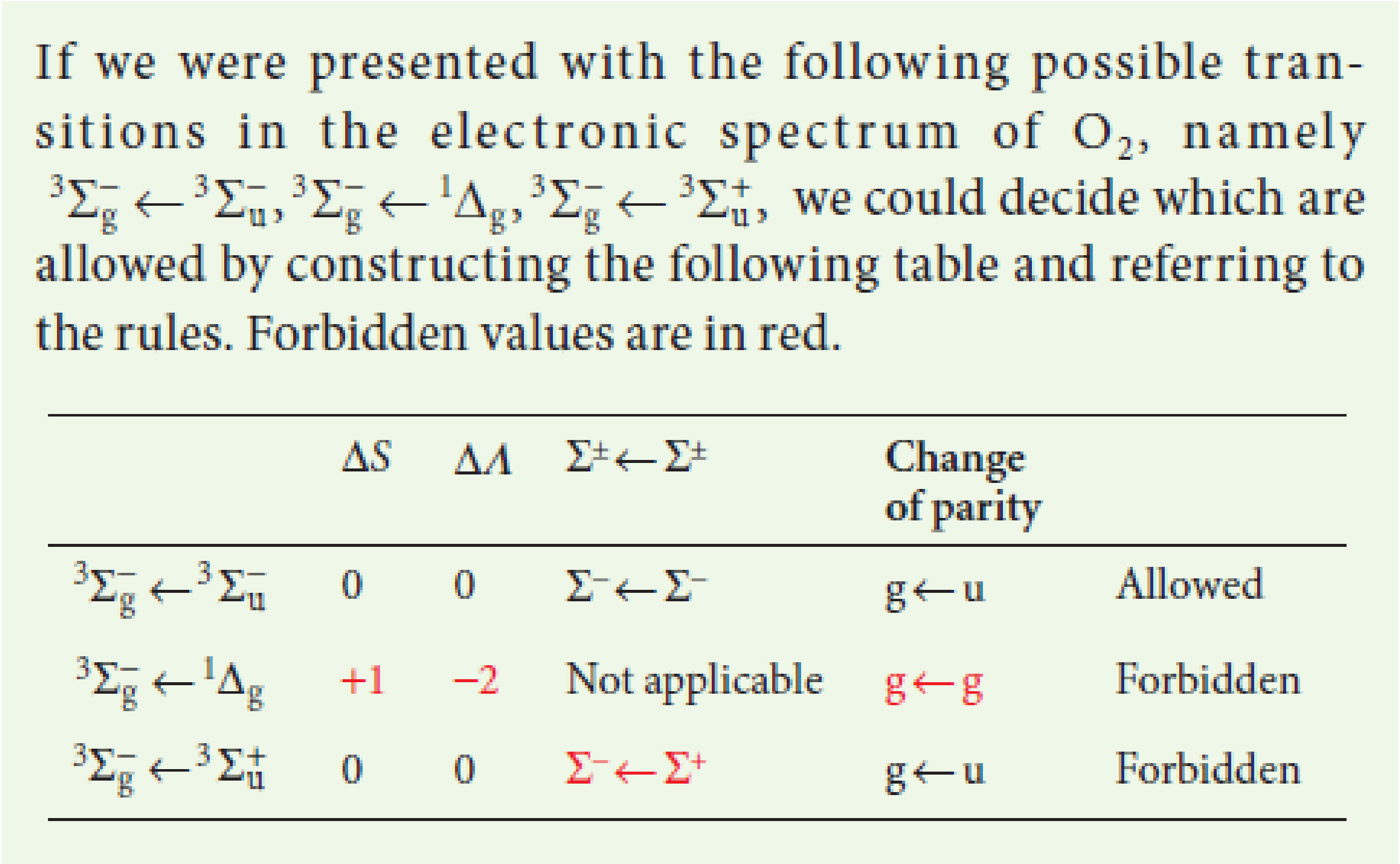
- Second, the *Laporte selection rule* for centrosymmetric molecules (those with a centre of inversion) states that *the only allowed transitions are transitions that are accompanied by a change of parity*. That is,
- For centrosymmetric molecules, only u → g and g → u are allowed.

A forbidden g → g transition can become allowed if the **centre of symmetry** is eliminated by an asymmetrical vibration, such as the one shown below. When the centre of symmetry is lost, g → g and u → u transitions are no longer parity forbidden and become weakly allowed. A transition that derives its intensity from an asymmetrical vibration of a molecule is called a **vibronic** transition.



A d-d transition is parity-forbidden because it corresponds to a g-g transition. However, a vibration of the molecule can destroy the inversion symmetry of the molecule and the g, u classification no longer applies. The removal of the centre of symmetry gives rise to a ***vibronically*** allowed transition.

Allowed Transition of O_2

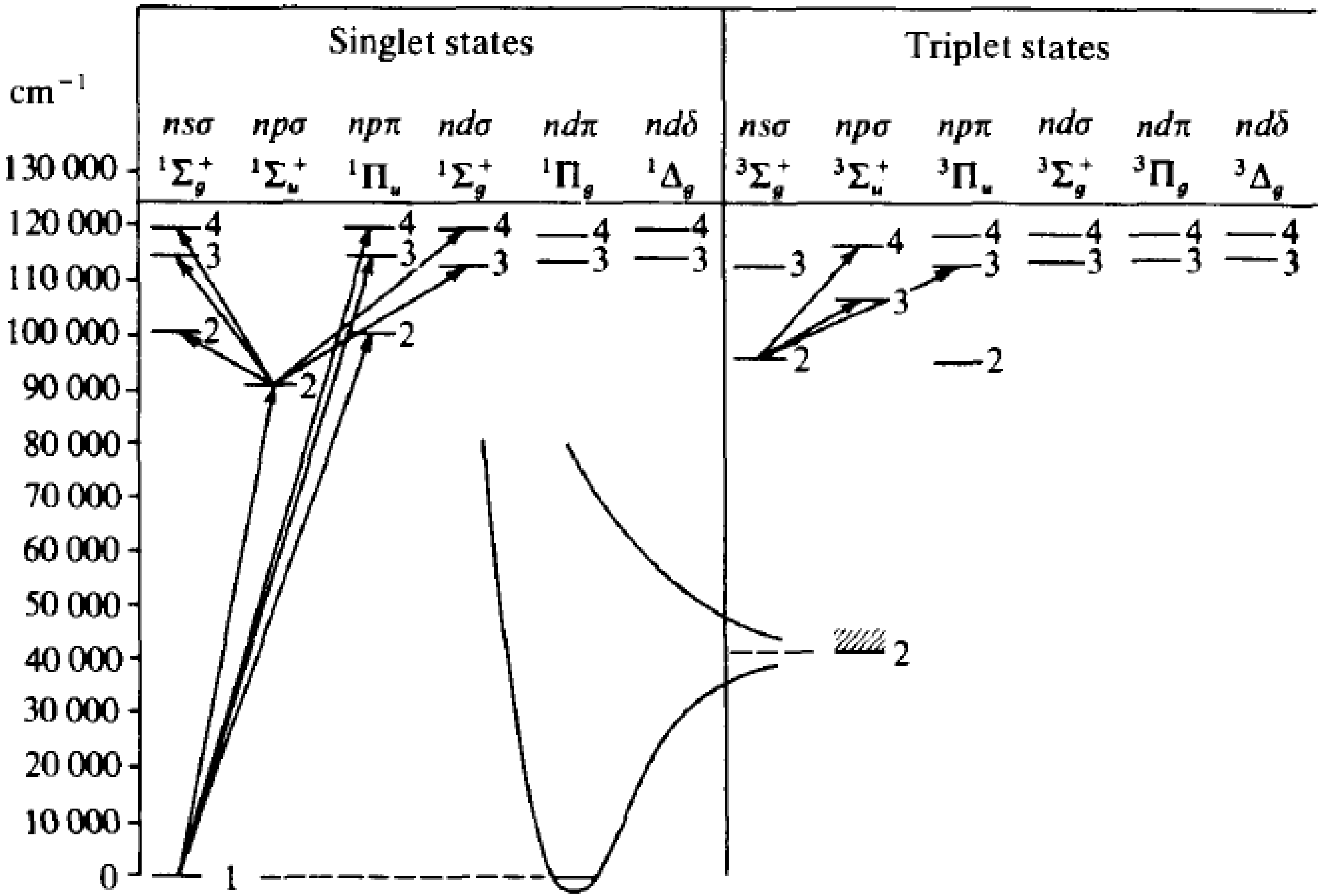


If we were presented with the following possible transitions in the electronic spectrum of O_2, namely $^3\Sigma_g^- \leftarrow {}^3\Sigma_u^-$, $^3\Sigma_g^- \leftarrow {}^1\Delta_g$, $^3\Sigma_g^- \leftarrow {}^3\Sigma_u^+$, we could decide which are allowed by constructing the following table and referring to the rules. Forbidden values are in red.

	ΔS	$\Delta\Lambda$	$\Sigma^\pm \leftarrow \Sigma^\pm$	Change of parity	
$^3\Sigma_g^- \leftarrow {}^3\Sigma_u^-$	0	0	$\Sigma^- \leftarrow \Sigma^-$	g←u	Allowed
$^3\Sigma_g^- \leftarrow {}^1\Delta_g$	+1	−2	Not applicable	g←g	Forbidden
$^3\Sigma_g^- \leftarrow {}^3\Sigma_u^+$	0	0	$\Sigma^- \leftarrow \Sigma^+$	g←u	Forbidden

Q. Which of the following electronic transitions are allowed in O_2: $^3\sum_g^- \leftrightarrow {}^1\sum_g^+ \; and \; ^3\sum_g^- \leftrightarrow {}^3\sum_u$?

Possible Transitions in Hydrogen molecule



Electronic Transition in Polyatomic Molecules

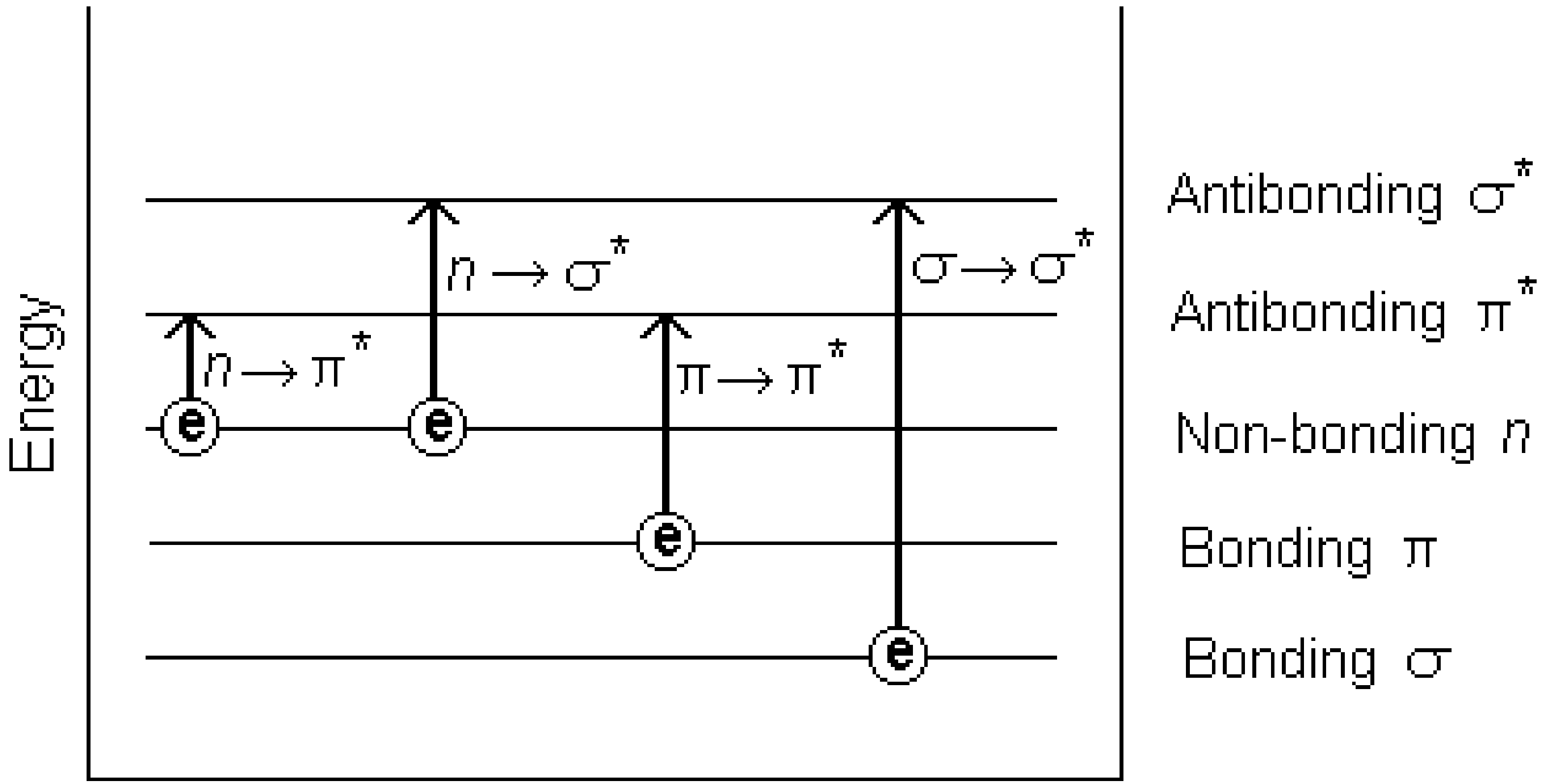
The absorption of UV or visible radiation corresponds to the excitation of outer electrons. There are three types of electronic transition which can be considered.

1. Transitions involving π, σ, and *n* electrons
2. Transitions involving charge-transfer electrons
3. Transitions involving *d* and *f* electrons

When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each other electronic level.

Electronic Transition in Polyatomic Molecules

Possible *electronic* transitions of π, σ, and *n* electrons are;



Transitions involving π, σ, and *n* electrons

$\sigma \rightarrow \sigma^*$ Transitions

An electron in a bonding σ orbital is excited to the corresponding antibonding orbital. The energy required is large. For example, methane (which has only C-H bonds, and can only undergo $\sigma \rightarrow \sigma^*$ transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to $\sigma \rightarrow \sigma^*$ transitions are not seen in typical UV-Vis. spectra (200 - 700 nm)

$n \rightarrow \sigma^*$ Transitions

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of $n \rightarrow \sigma^*$ transitions. These transitions usually need less energy than $\sigma \rightarrow \sigma^*$ transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in the UV region is small.

n → π^* and $\pi \rightarrow \pi^*$ Transitions

Most absorption spectroscopy of organic compounds is based on transitions of *n* or π electrons to the π^* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an unsaturated group in the molecule to provide the π electrons.

Molar absorbtivities from $n \rightarrow \pi^*$ transitions are relatively low, and range from 10 to100 L mol^{-1} cm^{-1}. $\pi \rightarrow \pi^*$ transitions normally give molar absorbtivities between 1000 and 10,000 L mol^{-1} cm^{-1} .

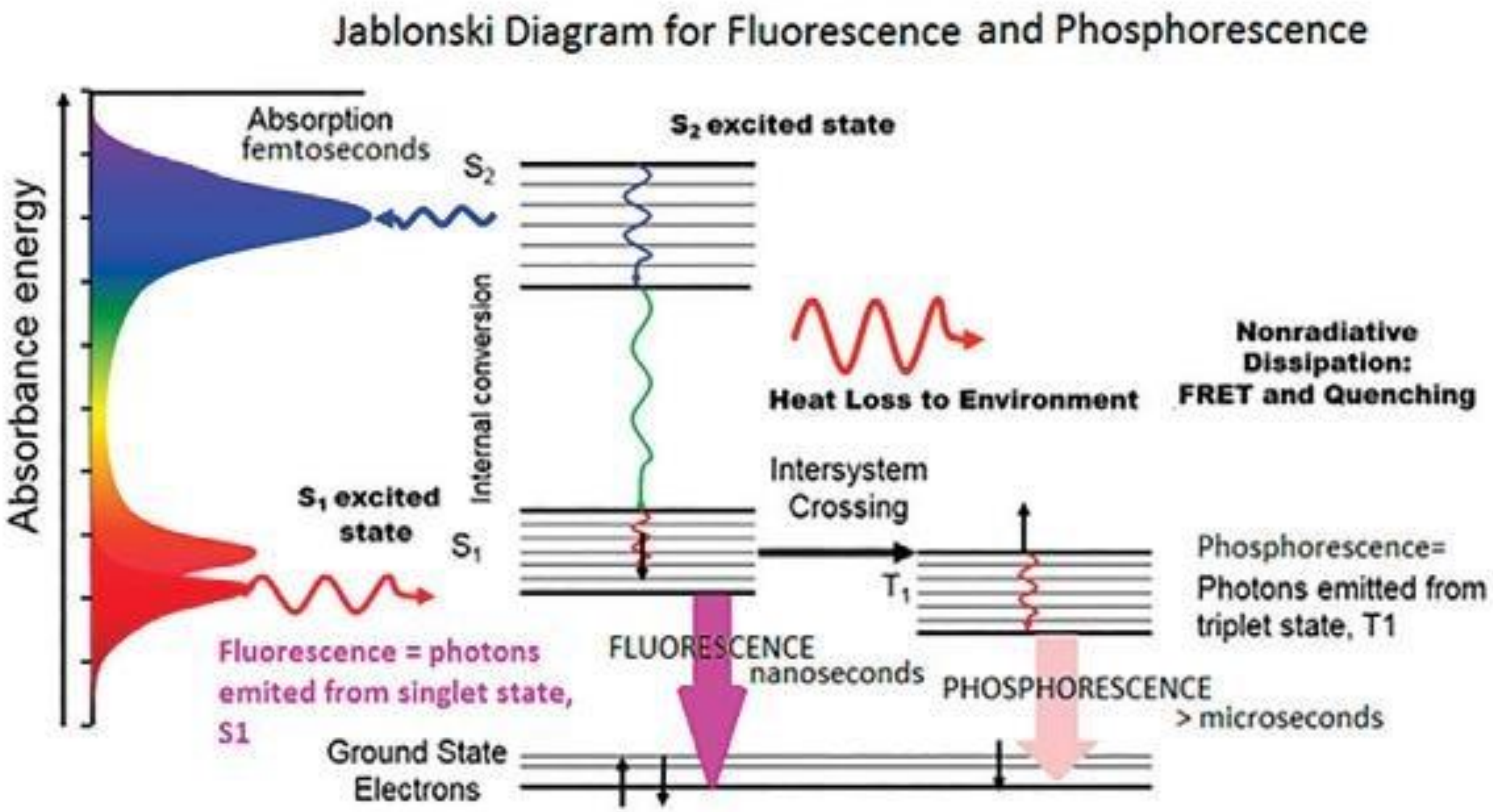
Charge - Transfer Absorption

Many inorganic species show charge-transfer absorption and are called *charge-transfer complexes*.

For a complex to demonstrate charge-transfer behaviour, one of its components must have electron donating properties and another component must be able to accept electrons. Absorption of radiation then involves the transfer of an electron from the donor to an orbital associated with the acceptor.

Molar absorbtivities from charge-transfer absorption are large (greater that 10,000 L mol^{-1} cm^{-1}).

Emission Spectra: Fluorescence and Phosphorescence



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Thank You