



Fig. 8.18 Electronic spectrum of benzene in solution

Table 8.10 Electronic absorption spectrum of benzene

Transition	Activity	Vibrational mode	Polarization	Absorption maximum
${}^1A_{1g} \rightarrow {}^1B_{2u}$	Vibronic	e_{2g}		256 (ϵ 200)
${}^1A_{1g} \rightarrow {}^2B_{2u}$	Vibronic	$e_{2g} + b_{2g}$		204 (ϵ 7 900)
${}^1A_{1g} \rightarrow {}^1E_{1u}$	Allowed		(x, y)	184 (ϵ 60 000)

the D_{6h} symmetry of the molecule is lowered. This would not be the case for E_{1u} since the transition ${}^1A_{1g} \rightarrow {}^1E_{1u}$ is fully allowed in D_{6h} symmetry. We are left with assignment of either B_{1u} or B_{2u} for the 256 nm band of benzene and the transitions to both these states are forbidden.

The benzene molecules constantly execute vibrations, some are symmetric and others are asymmetric, during which the symmetry of benzene will be lowered. Since electronic transitions are more rapid than molecular vibrations, benzene behaves with respect to light absorption as if it were a mixture of molecules of different symmetry, depending on their vibrational states. Since the amplitude of vibrations is small, the molecules behave approximately as if they had D_{6h} symmetry. Thus the first $\pi \rightarrow \pi^*$ transition is not completely forbidden for the individual molecules in vibrational states distorting D_{6h} symmetry, the transition remains of low intensity. Thus the weak band of benzene near 256 nm is a forbidden band which becomes weakly allowed because of vibrational interaction.

We now determine the vibrations activating the appearance of the ${}^1A_{1g} \rightarrow {}^1B_{2u}$ and ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transitions of benzene. The products of the representations of the dipole moment components and the excited electronic states of benzene are

$$\Gamma_{\mu} \Gamma_{ex} = (A_{2u} + E_{1u}) B_{1u} = B_{2g} + E_{2g}$$

$$\Gamma_{\mu} \Gamma_{ex} = (A_{2u} + E_{1u}) B_{2u} = B_{1g} + E_{2g}$$