

biphenyl.

2.11 Types of absorption bands

Following types of bands originate as a result of the possible transitions in a compound.

(a) **K*-Bands.** K-bands originate from a compound containing a conjugated system. Such type of bands arise in compounds like dienes, polyenes, enones *etc.* K-bands also appear in an aromatic compound which is substituted by a chromophore. The intensity of K-band, is usually more than 10^4 . The K-band absorption due

Table T₂—2. K-band Transitions

| Compound | Transition | (λ_{max} in μ) | ϵ_{max} |
|----------------------------|-------------------------|------------------------------|------------------|
| Butadiene 1,3 | $\pi \rightarrow \pi^*$ | 217 | 21,000 |
| Acrolein** | $\pi \rightarrow \pi^*$ | 210 | 11,500 |
| Styrene** | $\pi \rightarrow \pi^*$ | 214 | 12,000 |
| Acetophenone | $\pi \rightarrow \pi^*$ | 240 | 13,000 |
| 2, 3 dimethyl butadiene | $\pi \rightarrow \pi^*$ | 226 | 21,400 |
| Pentadiene 1, 3 | $\pi \rightarrow \pi^*$ | 223 | 22,600 |

*Konjugierte—German.

**For acrolein, styrene, acetophenone *etc.*, bands other than K-bands also appear,

to conjugated 'enes' and 'enones' are effected differently by changing the polarity of the solvent.

(b) **R*band**. Such type of bands originate due to $n \rightarrow \pi^*$ transition of a single chromophoric group and having at least one lone

Table T₂—3. R-band Transitions

| Compound | Transition | $\lambda_{max}(m\mu)$ | ϵ_{max} |
|---------------------|-----------------------|-----------------------|------------------|
| Acetone | $n \rightarrow \pi^*$ | 279 | 15 |
| Acetaldehyde | $n \rightarrow \pi^*$ | 293 | ~12 |
| Acrolein | $n \rightarrow \pi^*$ | 315 | 14 |
| Acetophenone | $n \rightarrow \pi^*$ | 319 | 50 |
| Methyl Vinyl Ketone | $n \rightarrow \pi^*$ | 320 | ~14 |
| Crotonaldehyde | $n \rightarrow \pi^*$ | 322 | ~14 |

pair of electrons on the hetero atom. R-bands are also called **forbidden bands**. These are less intense with ϵ_{max} value below 100.

(c) **B-band**. Such type of bands arise due to $\pi \rightarrow \pi^*$ transition in aromatic or hetero-aromatic molecules. Benzene shows

Table T₂—4. B-band Transitions

| Compound | Transition | $\lambda_{max}(m\mu)$ | ϵ_{max} |
|---------------|---------------|-----------------------|------------------|
| Benzene | $\pi - \pi^*$ | 255 | 215 |
| Styrene | $\pi - \pi^*$ | 282 | 450 |
| Toluene | $\pi - \pi^*$ | 262 | 174 |
| Phenol | $\pi - \pi^*$ | 270 | 1450 |
| Acetophenone | $\pi - \pi^*$ | 278 | 1110 |
| Benzaldehyde | $\pi - \pi^*$ | 280 | 1500 |
| Benzoic acid | $\pi - \pi^*$ | 270 | 800 |
| Nitro-benzene | $\pi - \pi^*$ | 280 | 1000 |
| Naphthalene | $\pi - \pi^*$ | 312 | 289 |
| Quinoline | $\pi - \pi^*$ | 315 | 2500 |

absorption peaks between 230–270 $m\mu$. When a chromophoric group is attached to the benzene ring, the B-bands are observed at longer wave-lengths than the more intense K-bands. For example, K-band appears at 244 $m\mu$, ϵ_{max} 12000 and B-band at 282 $m\mu$, ϵ_{max} 450. Out of K, B and R-bands which appear in the spectrum of an aromatic compound, K-band appears at a longer wave-length. For example, in acetophenone R-band ($n \rightarrow \pi^*$, forbidden) appears at

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R-band or $n \rightarrow \pi^$ transition is most characteristic for a carbonyl group of aldehyde or ketone. For aldehydes, it usually appears at higher wave-lengths compared to a ketone but at lower value of ϵ_{max}

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319 $m\mu$ ϵ_{max} 50 while K and B-bands appear at 240 and 278 $m\mu$ respectively. The fine spectrum of B-band in case of

- (i) substituted aromatic compounds and
 - (ii) by the use of polar solvents
- may be missing.

(7) **E-bands.** Such bands originate due to the electronic transitions in the benzenoid system of three ethylenic bonds which are in closed cyclic conjugation. These are further characterised as

Table T₂—5. E-band Transitions

| Compound | E ₁ -band | | E ₂ -band | |
|-------------|-------------------------------|------------------|-------------------------------|------------------|
| | λ_{max} ($m\mu$) | ϵ_{max} | λ_{max} ($m\mu$) | ϵ_{max} |
| Benzene | 184 | 30,000 | 204 | 79,00 |
| Naphthalene | 221 | 133,000 | 286 | 9,300 |
| Anthracene | 256 | 180,000 | 375 | 9,000 |
| Pyrrole | 234 | 10,800 | 288 | 760 |
| Thiophene | ~270 | 6,300 | ~294 | 600 |
| Quinoline | 288 | 40,000 | 270 | 3,162 |

E₁ and E₂-bands. E₁ and E₂ bands of benzene appear at 184 and 204 $m\mu$ respectively. E₁ band which appears at lower wave-length is usually more intense than the E₂-band for the same compound which appears at longer wave-length.

Solvent Effects

It has been found that increase in polarity of the solvent generally shifts $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands to shorter wavelengths and $\pi \rightarrow \pi^*$ bands to longer wavelengths.

Following points may also be noted in connection with the effect of solvent polarity on the various types of bands.

(i) **K-band.** The K-band absorption due to conjugated 'enes' and 'enones' are effected differently by changing the polarity of the solvent. Usually, K-bands due to conjugated dienes are not effected by changing the polarity of the solvent while these bands due to 'enones' show a red shift by increasing the polarity of the solvent.

(ii) **R-band.** The absorption shifts to lower wavelength (blue shift) with the increase in polarity of the solvent.

(iii) **B-band.** The position as well as the intensity of the B-band is not shifted by increasing the polarity of the solvent. But in heterocyclic aromatic compounds, a marked hyperchromic shift (increase in ϵ_{max}) is observed by increasing the polarity of the solvent.

2.13 Conjugated dienes

The wave-length of absorption is shifted to higher values (Bathochromic shift), if two or more chromophoric groups are present in conjugation in a molecule. For example, ethylene (one double bond) absorbs at $170m\mu$ ($\pi \rightarrow \pi^*$ transition) while butadiene (two double bonds in conjugation) absorbs at $217 m\mu$. The bathochromic shift is more pronounced if the double bonds are in conju-