

Solvent Effects on UV/Vis Spectra: Benzophenone.

In going from a nonpolar to a polar solvent, the $\pi \rightarrow \pi^*$ absorption undergoes a bathochromic shift, while the $n \rightarrow \pi^*$ absorption undergoes a hypsochromic shift. This contradictory behavior of the absorption bands with changes in solvent polarity is illustrated for benzophenone in the table and the figure below. This feature is diagnostic to distinguish between these types of absorptions in carbonyl compounds. Explain this important feature.

Table 6-3. The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ band maxima in the UV/Vis absorption spectrum of benzophenone in solvents of increasing polarity [104].

Solvents	$\tilde{\nu}(n \rightarrow \pi^*)/\text{cm}^{-1}$	$\tilde{\nu}(\pi \rightarrow \pi^*)/\text{cm}^{-1}$
<i>n</i> -Hexane	28860	40400
Cyclohexane	28860	40240
Diethyl ether	29070	40160
1,2-Dichloroethane	29370	39600
Dimethyl sulfoxide	29370	—
<i>N,N</i> -Dimethylformamide	29330	—
Acetonitrile	29540	39920
1-Butanol	29990	39600
1-Propanol	29900	39600
Ethanol	30080	39680
Methanol	30170	39600
Water	ca. 31060 (sh)	38830

$$\Delta\tilde{\nu} = -2200 \text{ cm}^{-1} \quad \Delta\tilde{\nu} = 1570 \text{ cm}^{-1}$$

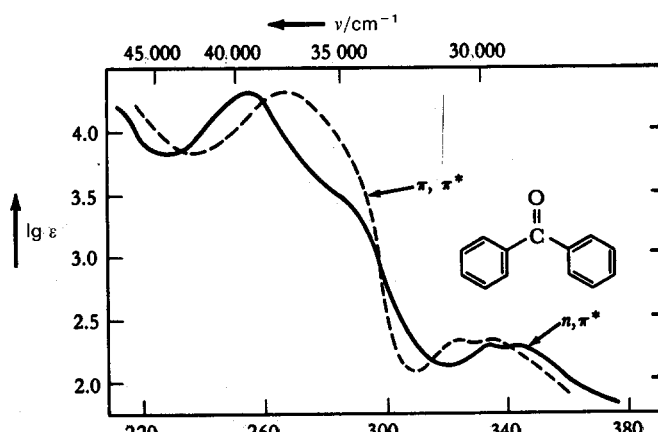


Fig. 6-6. UV/Vis absorption spectrum of benzophenone in cyclohexane (—) and ethanol (---) at 25 °C [104, 108].