

First experimental evidence for the existence of blue-shifted iodine band: The ${}^3\pi_1-{}^1\Sigma^+$ transition. An anecdote

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Abstract. The absorption maximum of the ${}^3\pi_1-{}^1\Sigma^+$ transition of the iodine molecule in cyclohexane is found to be at 689 nm. Derivative spectroscopic evidence for the blue shift of the above band in complexed iodine has been provided for the first time.

Keywords. Iodine band; complexed iodine visible band; blue-shifted iodine band.

Several studies of the iodine visible bands in solutions were reported (Ham 1954; Nagakura 1958; Voigt 1968; Mulliken and Person 1969; Rao *et al* 1971; Tamres and Bhat 1971; Tamres 1973). The visible absorption of the iodine molecule arises due to electron transitions from the ground state, ${}^1\Sigma^+$, to the excited state, ${}^3\pi_0^+$ and ${}^3\pi_1$. Charge transfer complexes of iodine in solution show a characteristic blue shift of the iodine visible band (~ 520 nm in nonpolar solvents). Mulliken and Person (1969) were of the opinion that the antibonding orbital in iodine has a larger effective size than the ground state orbital, and the blue shift can be attributed to the larger exchange repulsion between the iodine molecule in the excited state and the adjacent donor. Based on this, one would expect to see the blue shift in the weaker absorption maximum (~ 690 nm, ${}^3\pi_1-{}^1\Sigma^+$) also. However, inspite of several attempts made by many researchers, there is no evidence for the existence of the second blue-shifted iodine visible band (~ 520 nm in nonpolar solvents). Mulliken and Person (1969) were Voigt 1968; Mulliken and Person 1969). The failure to locate the blue shift is probably due to the shape of the uncomplexed iodine band (shoulder) and the not significant variation in the band position and intensities. We anticipated that use of more favourable experimental conditions would be conducive to the observation of the blue shift. Accordingly, employing more favourable experimental conditions namely, very high donor concentrations and making use of derivative spectroscopy, we, for the first time, observed the blue shift of the second band maximum of iodine (690 nm; ${}^3\pi_1-{}^1\Sigma^+$) in the range of 682–675 nm for iodine complexes of benzene, toluene and xylenes.

Measurements of the spectrum of iodine in cyclohexane solution shows a 'shoulder' at ~ 690 nm (in addition to the 520 nm band) and the half-band width of this 'resolved' band (with λ_{\max} 689 nm) is at $3014 \pm 50 \text{ cm}^{-1}$. However, the second derivative of this 'hidden' peak shows the absorption minimum (corrected for the slight shift due to the

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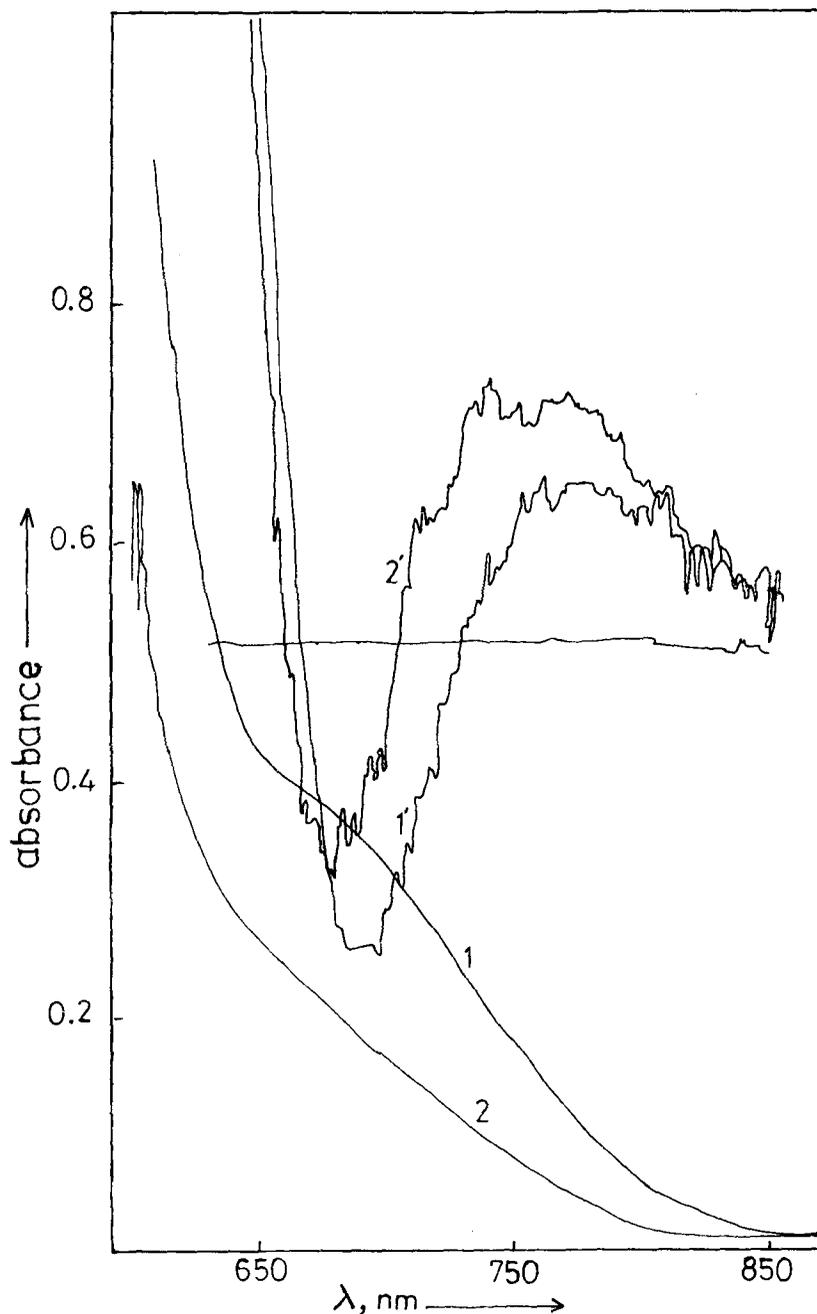


Figure 1. Normal (1 and 2) and derivative (1' and 2') spectra of iodine and iodine-benzene in cyclohexane. 1 and 1' - Iodine alone; 2 and 2' - complexed iodine.

differentiation process) at 689 ± 1 nm. This band has been ascribed to the ${}^3\pi_1-{}^1\Sigma^+$ transition (Mulliken and Person 1969). When iodine was complexed with benzene, toluene, *o*-, *m*- and *p*-xylenes, the 689 nm band of iodine shifts to lower wavelengths and the second derivatives of the spectra appear at 682, 680, 678, 675 and 675 ± 2 nm

respectively (figure 1). The half-band widths of the resolved absorption bands are at $\sim 2900 \pm 80 \text{ cm}^{-1}$ (the half-band width of the first blue-shifted iodine band for the above systems had increased from 3250 cm^{-1} to $3300\text{--}3500 \text{ cm}^{-1}$, Shedbalkar and Bhat 1984). The donor concentration was about 10,000 times higher than that of iodine. Therefore, it is reasonable to assume that almost all the iodine was in complexed form and the observed band maximum can be ascribed to the complexed iodine alone.

The σ_u antibonding molecular orbital which contains the electron excited by the absorption of light in the visible band must be larger than the occupied MO in the normal state of I_2 . When an iodine molecule, which is paired off with a close partner in a complex, is excited by absorption of visible light, its suddenly swollen size increases the repulsion energy between it and the donor. This repulsion energy, which should be greater the more intimate the complex, is added to the usual energy of the excited iodine molecule giving rise to a blue shift in the absorption frequencies. Therefore, the blue shift should become larger with the increasingly closer contact between the donor and iodine. So, the magnitude of the blue shift of the iodine band should correlate well with the electron-donor ability of the donor molecules and that is what has been observed in the present case.

The intensity (i.e. the molar extinction coefficient) of the second visible band of iodine decreases after complexation ($\epsilon_{690}^{\text{free}}\text{I}_2 = 45 \pm 3 \text{ dm}^3 \text{ mol}^{-1} \text{ m}^{-1}$; $\epsilon_{682}^{\text{comp}}\text{I}_2 = 36 \pm 3 \text{ dm}^3 \text{ mol}^{-1} \text{ m}^{-1}$ after correction) whereas the intensity of the first visible band of iodine (i.e. the 520 nm band), increases from $980 \text{ dm}^3 \text{ mol}^{-1} \text{ m}^{-1}$ to $1100 \text{ dm}^3 \text{ mol}^{-1} \text{ m}^{-1}$ (Tamres and Bhat 1971; Shedbalkar and Bhat 1984).

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