

❖ Electronic Spectra of Molecular Addition Compounds

The electronic absorption spectra of molecular addition compounds can be best understood by considering the example of iodine adducts. The absorption maxima for iodine (dissolved in carbon tetrachloride) appears at about 520 nm wavelength. This band, without any doubt, can successfully be assigned to a $\pi^* \rightarrow \sigma^*$ transition; and is also responsible for the violet color of free iodine. However, when certain ligands like macrocyclic ethers or any other donor molecules are added to the iodine solution, two obvious changes in the absorption spectrum occur. The characteristic band of free iodine shows a blue shift, and some intense peaks arise in the ultraviolet region. The hypsochromic shift is due to the complexation of free iodine, while the origin of additional peaks in the ultra-violet region can be ascribed to the charge transfer transitions. The later claim is also confirmed by the absence of any dominant peak in the absorption spectra of the ligand alone. Furthermore, the isobestic point at 490 nm suggests the presence of two absorbing species in the system; and the value of the equilibrium constant K obtained over a wide range of base concentrations also demonstrates the existence of a 1:1 molecular addition compound.

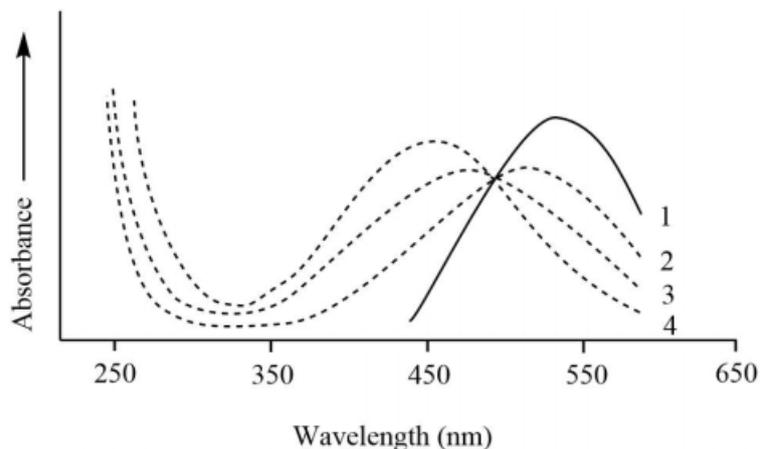


Figure 76. The UV-visible absorption spectra of iodine (1) and base-iodine solutions in CCl_4 with increasing concentration of base ($2 < 3 < 4$).

The observed blue shift in the free iodine band is due to the perturbation of σ^* molecular orbital of iodine by a repulsive interaction between the two components of the charge-transfer complex. Therefore, as the repulsive interactions increase, a larger blue shift of the iodine band would be expected. Hence, it is sensible to consider the amount of the hypsochromic shift in the free I_2 band as a measure of the interaction between the iodine molecule and the ligand molecule. The limiting value of the blue shift is approximately 360 nm and which is the characteristic absorption peak for I_3^- ions. The formation of triiodide ion, implicitly, would mean that the magnitude of the polarization of the iodine molecule in base-iodine complex is so large that a clear-cut charge separation has occurred. However, the confirmation of I_3^- ions in solution must be done by checking the presence of the second characteristic peak of triiodide ion at 292 nm.

The absorption spectra of I_2 in the presence of large excess of dicyclohexyl-18-crown-6 in chloroform solution at is shown in 'Figure 77'. It can clearly be seen that none of the initial reactants show any measurable absorption in 250-450 nm region, however, the addition of crown ether to the iodine solution generates in two strong absorptions bands the aforementioned wavelength range. This can be attributed to the formation of charge-transfer complexes between the dicyclohexyl-18-crown-6 and the free iodine which causes the vanishing of purple color from the solution. The spectra recorded for the electron donor-acceptor (EDA) complex between ligands and I_2 are time-dependent and the intensities of the different absorptions change significantly with time. Though the general profile of the spectra remains unaffected, after some time the purple color of solution begins to disappear slowly and the intensity of the absorption bands in the 250–600 nm region declines with time.

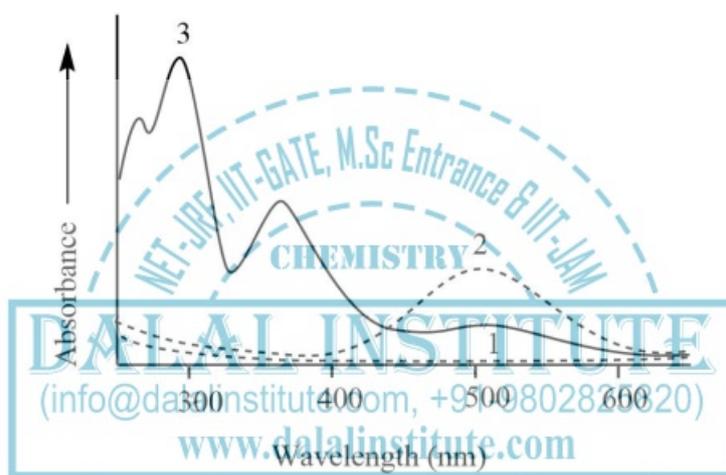


Figure 77. The UV-visible absorption spectra of I_2 in the presence of excess of dicyclohexyl-18-crown-6.

If ψ_{cov} includes contributions from covalent interactions while ψ_{ele} includes contributions from purely electrostatic forces (these are described as charge-transfer interactions); then the bonding in iodine adducts can be described by the equation:

$$\psi = a\psi_{cov} + b\psi_{ele}$$

The ground state of most adducts exists with $b > a$; however, as the charge-transfer transition occurs, the situation is actually reversed with $a > b$. This results in a band around 250 nm owing to the transition in which an electron from the ground state is promoted to an excited state. Hence, the assignment of the charge-transfer band can be approximated by a transfer of an electron from the nonbonding orbital of the base to the σ^* orbital iodine. The whole spectra (including normal $\pi^* \rightarrow \sigma^*$ transition after complexation) can be explained in terms of relative energies of the molecular orbitals of iodine and the complex. The molecular orbitals ($\sigma_{complex}$, $\sigma^*_{complex}$, and $\pi^*_{complex}$) are very much like the original base and iodine orbitals because of the weak Lewis acid-base interaction.

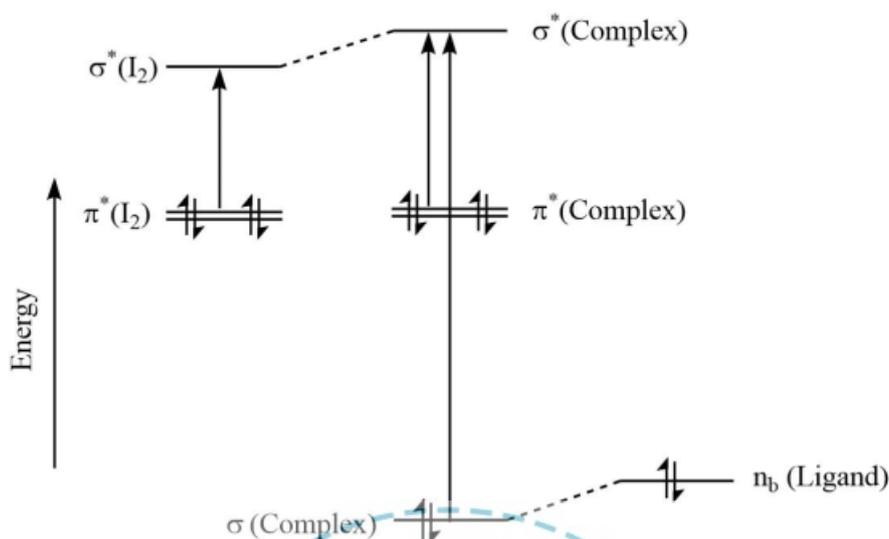


Figure 78. The partial molecular orbital diagram in base-iodine adducts.

Meanwhile, $\sigma^*_{\text{complex}}$ is slightly higher in energy than the corresponding σ^*_{iodine} , the analogous transition in complexed iodine requires slightly more energy than the corresponding transition in free and a blue shift is observed. The charge-transfer transition occurs at higher energy in the ultraviolet region. The claim that the blue shift is correlated to the magnitude of the base-iodine interaction (enthalpy of formation of adduct) would be reasonable only if the energy of π^*_{complex} differs very little from that of π^*_{iodine} or its energy changes with the enthalpy in a linear fashion. When a wide range of different types of Lewis bases were studied with iodine solution, it has been found that the abovementioned correlation does exist roughly but is not of quantitative nature. The equation relating the charge transfer band, the ionization energy of the base, I_b , and the electron affinity of the acid, E_a , has also been reported:

$$\nu_{\text{charge transfer band}} = I_b - E_a - \Delta$$

where Δ is an empirically determined constant for a related series of bases.

Both inorganic and organic researchers have always been interested in the enthalpies for the formation of these charge-transfer complexes. This is because a lot of information about donor and acceptor interactions can be obtained which is pretty much essential to an understanding of many phenomena in inorganic systems; especially in the areas of non-aqueous solvents and coordination chemistry. It should also be noted that the thermodynamic study of these adducts is easier in the solvents like hexane or carbon tetrachloride than in polar solvents, which is due to the larger magnitude of enthalpies and entropies of solvation in the later. The characteristic results from ligand-iodine solutions with minimal solvation effects for a wide range of systems can be studied and the information that can be obtained by studying enthalpies of association in weakly basic, non-polar solvents are given below:

1. A correlation of the heat of formation of iodine adducts of a series of para-substituted benzamides with the Hammett substituent constants of the benzamides.
2. The donor properties of the π -electron systems of alkyl-substituted benzenes
3. The donor properties of sulfites, sulfoxides, sulfones, and carbonyl compounds have been studied which shows that carbon-oxygen bonding in ketones and acetates is more effective than in sulfur-oxygen bonding.
4. The ring size effect on the donor properties of cyclic ethers and sulphides showed that for $(\text{CH}_2)_n \text{S}$, donor strength of sulfur follows order $n = 5 > 6 > 4 > 3$; and the order for the corresponding ethers is $4 > 5 > 6 > 3$.
5. The donor strength of 3° , 2° , and 1° amines have been assessed which varies with the acid studied.

Besides iodine, a lot of charge-transfer complexes of many other Lewis acids absorb light in the UV-visible region. The factors affecting the magnitude of the interaction and other useful information regarding the bonding in the molecular addition compounds of SO_2 , ICI , Br_2 , phenol and other acids have also been investigated.



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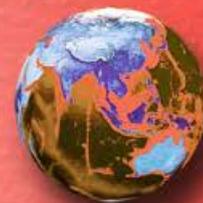
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Volume I

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