NOTES Bull. Chem. Soc. Jpn., 54, 1561—1562 (1981)

Anomalous Solvatochromism of Charge-transfer Absorption Bands

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(Received May 15, 1980)

Synopsis. When n-donor solvents are employed, charge-tansfer absorption bands become broader on the low-energy side, the absorption peaks shifting toward the high-energy side. This type of solvatochromism has an analogy with that of the n-π^* transitions.

Despite continued interest in the charge-transfer (CT) complexes in the solution phase, various aspects of the electronic spectra remain unclarified.[1-3] As Offen and Abidi pointed out,[1] no current theory of solvatochromism can be applied assuredly to the CT absorption bands. In order to solve the problem, the absorption spectra of weak CT complexes were reexamined in various solvents. It was found that the CT absorption band changes with solvent. An attempt was made to interpret this phenomenon in terms of specific solvation.

In general, unsubstituted aromatic hydrocarbons are suitable as donor components for the study of solvent effects on binary CT complexes. Bulky substituents of the donor molecule suppress solvatochromism to some extent.[4] Naphthalene and tetracyanoethylene (TCNE) best illustrate the donor-acceptor pair for the present purpose. Figure 1 shows the electronic absorption spectra of the naphthalene–TCNE complex in four solvents. The first two absorption bands appear in the visible region, and have been assigned to the CT transitions from naphthalene to TCNE.[5] These CT bands are usually asymmetric in appearance.[6]

The peak of the first CT band moves in a wide range when the solvent is changed. There is an absorption peak at 17670 cm^{-1} in carbon disulfide while it shifts to 19800 cm^{-1} in acetonitrile. The difference in energy amounts to 2100 cm^{-1}. The peaks in the 1,2-dichloroethane and bromoethane solutions are located halfway at 18170 and 18940 cm^{-1}, respectively. Despite such a large displacement of the peak position, the absorption edge remains in almost the same position, light absorption beginning at *ca.* 14500 cm^{-1} in each solution. All solutions of the complex do not exhibit the absorption edge here; in solvents, such as hexane, cyclohexane, ethyl acetate, and methanol, the absorption edge shifts to *ca.* 15500 cm^{-1}. However, such a displacement of the edge is small as compared with that of the absorption peak. The first absorption peaks are located at 18980 cm^{-1} in hexane, at 18520 cm^{-1} in cyclohexane, at 20200 cm^{-1} in ethyl acetate, and at 20530 cm^{-1} in methanol. Consequently, broadening of the entire absorption band occurs as the peak position is displaced to the higher-energy side.

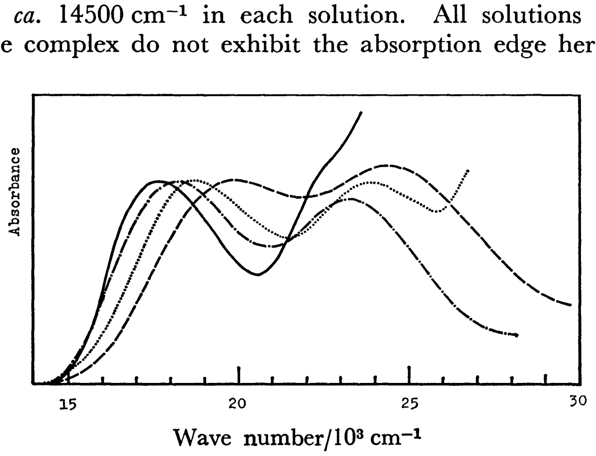

Fig. 1. Absorption spectra of the naphthalene–TCNE complex in carbon disulfide (——), 1,2-dichloroethane (—·—), bromethane (······), and acetonitrile (——).

When hydrocarbon solvents, such as hexane and cyclohexane, are used, the absorption peak apparently follows the dielectric theory of solvatochromism.[2,7] However, most other solvents affect the CT band in quite a different manner. Even when a solvent has a large dielectric constant, it often gives rise to a large blue shift of the CT absorption band.[1-3] If we consider that a weak CT complex has a larger dipole moment in the excited state than in the ground state,[5] this is obviously inconsistent with the theory of solvatochromism described in terms of the refractive index and the dielectric constant of the solvent.[8] It is evident that the solvent dependence of the CT absorption band cannot be applied to the determination of the dipole moment of the excited-state complex by means of the dielectric theory.[9]

The absorption edge is closely related to the 0–0 vibronic level of the electronic transition. The first absorption band of the naphthalene–TCNE complex in the gas phase begins at 16900 cm^{-1} with a peak at 21100 cm^{-1}.[2] The edge shifts to the low-energy side by 2400 cm^{-1} when the complex is dissolved in the solvents given in Fig. 1; this indicates that both the 0-0 and higher vibronic levels move to the red in these solvents. The solvent shift caused by the dielectric effect, if any, should thus be evaluated as an energy shift of a certain (*i.e.*, fixed) vibronic level.

In principle, the absorption peak is related to the Franck-Condon (*i.e.*, vertical) transition. The shift of the CT absorption maximum along with the deformation of the band shape is determined mainly by the variation of the Franck-Condon transition level. It is evident that the first band maximum of the naphthalene–TCNE complex does not always represent a fixed vibronic level (Fig. 1). It is likely that the 0-1 vibronic level is the strongest in saturated-hydrocarbon solvents.[10] However, it seems that the higher vibronic levels are more intense in the other solvents although they are blurred. A plausible vibrational mode taking part in the first CT band of the naphthalene–TCNE complex is an intramolecular vibration with a frequency of about 1300 cm^{-1} in the excited state. The frequency was estimated from the fine structure in the CT bands of the saturated-hydrocarbon solutions.[10]

The systematic study so far carried out on weak CT complexes has enabled us to distinguish n-donor solvents from other ones. Nagy *et al.* found that the n-donor solvents markedly shift the CT absorption band to the blue, and that the electron-donating power of the solvent is primarily responsible for the anomalous blue shift.[3] In line with this, the present observation revealed that the broadening of the CT band is conspicuous in such n-donor solvents as acetonitrile, ethyl acetate, and methanol. Therefore, it seems that the variation of the Franck-Condon envelope is substantially due to the coordination of n-donor-solvent molecules to the CT complex in the ground state.[3]

For example, acetonitrile is highly polar, and the molecular dynamics is highly anisotropic in the neat liquid.[11] An antiparallel arrangement seems to be the most probable orientational arrangement in acetonitrile. The acetonitrile molecules would, likewise, tend to be coordinated selectively to TCNE, since the C≡N bond moment of TCNE (3.6 D)[12] is comparable to the overall dipole moment of acetonitrile (3.92 D),[13] and acetonitrile has a large n-donor ability.[3,14] This suggests that the variation of the Franck-Condon envelope can be induced essentially by the solvation of the acceptor part (*i.e.*, TCNE). Thus, the vibrational mode which contributes to the first CT band of the naphthalene–TCNE complex might be ascribed to TCNE.

The above explanation is in line with that of McConnell[15,16] given to the blue shift of the n-π^* transitions, in which he states that the blue shift originates from the solvent molecules orienting themselves around the solute molecule to fit in with the ground-state charge distribution of the solute molecule. On excitation, if the charge distribution of the solute changes drastically (as in the case of n-π^* transitions and CT transitions alike), the solvent molecules would not have the position and orientation to bind most strongly with the excited-state charge distribution. This would give rise to the blue-shift phenomenon, since (relative to a saturated-hydrocarbon solvent) an n-donor solvent would give a greater solvation energy for the ground state of the solute than for the excited state. The resulting absorption peak would become much higher in energy than the relaxed excited state. This would give rise to the broadening of the absorption band on the low-energy side.

In conclusion, the anomalous blue shift, accompanied by band broadening, is commonly observed in the absorption spectra of weak CT complexes in solution. This blue-shift phenomenon seems to have caused great confusion in the analysis of solvent shifts.[1–3,9]

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