The Vibrational Structure of the Charge-Transfer Band in Solution

Jun-ichi AIHARA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

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Several authors have reported the existence of a vibrational structure in the absorption spectra of charge-transfer (CT) complexes in the solid state, while the solution spectra of the complexes are generally likely to be continuous.[1,2] No one has yet observed the fine structure in the solution spectra, though we have no definite evidence for its absence.[3]

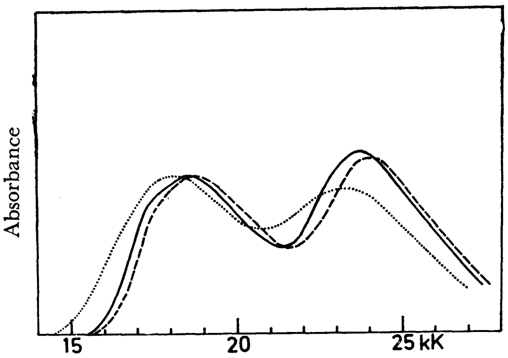

Fig. 1. Absorption spectra of the naphthalene-TCNE complex in cyclohexane (——), in n-hexane (------), and in methylene chloride (······).

Recently, we undertook a further investigation of the solution spectra of the CT complexes; partial success has been achieved in detecting some structure in the solution spectra of the naphthalene-tetracyanoethylene (TCNE) complex. Figure 1 shows typical CT absorption spectra of the naphthalene-TCNE complex in solution. This complex is known to have two CT absorption bands which correspond to the transitions from the highest and the second-highest filled orbital of naphthalene to the lowest vacant orbital of TCNE.[4]

We first found some anomaly on the low-energy side of the first CT band in n-hexane. The absorption maximum is preceded by a distinct shoulder; the locations are at 18800 and 17500 cm^{-1} respectively. The separation between them is approximately 1300 cm^{-1}, the uncertainty of this figure being ±100 cm^{-1}. The spectrum of the cyclohexane solution has a close resemblance to that of the n-hexane solution. A similar situation is also found among other saturated hydrocarbon solutions of this complex. The spacings are approximately equal in these solvents. These are listed in Table 1.

TABLE 1. ABSORPTION MAXIMA AND SHOULDERS OF THE FIRST CT BAND OF THE NAPHTHALENE-TCNE COMPLEX IN VARIOUS SOLVENTS (cm^{-1})

Solvent	Maximum	Shoulder	Difference
n-Hexane	18800	17500	1300
n-Heptane	18800	17400	1400
Cyclohexane	18500	17200	1300
Methylcyclohexane	18600	17300	1300

On the other hand, the majority of the solvents do not cause such a distinct structure in the CT spectra. As is exemplified in Fig. 1, the spectrum in methylene chloride appears very continuous and structureless, as usual. Various solvents, classified as benzenes, haloalkanes, ethers, and alcohols, do not induce such a structure. Hence, the appearance of the shoulder is confined to the saturated hydrocarbon solutions.

What is the origin of such a structure? The possibility of a third CT band in this region can be precluded as was recently proved by photoelectron spectroscopy and by theoretical calculations.[4,5] It seems that this structure is not due to another rotational isomer, either, in view of the fact that the second CT band is not accompanied by such a shoulder before the peak. The structure is characteristic of only the first CT band. Accordingly, we concluded that the fine structure originates from the vibronic interaction of the charge-transfer transition with the vibrational mode belonging to either the donor or the acceptor molecule. This presumption seems acceptable, though doubts may be voiced. It is not necessary to take the vibration of the donor against the acceptor into consideration, since the frequency of this mode is expected to be 100—200 cm^{-1}.[3]

Another support for this came from the fact that there exists a similar vibrational structure in the photoelectron spectrum of the molecular naphthalene.[5] When naphthalene is photo-ionized by the 584-Å radiation, a distinct 1410 cm^{-1} progression appears in the spectrum of the photoelectrons from the uppermost filled orbital. It is missing in that from the second highest filled orbital. This parallelism is quite consistent, since the ionization process of naphthalene is also involved in the charge-transfer transition of the naphthalene-TCNE complex.

As has been mentioned above, we could detect the fine structure of the CT bands in solution very rarely. However, its finding at all effectively aids the analysis of the electronic structure of the CT complex in solution. We will go on to examine the absorption spectra of other CT complexes in solution.

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