Absorption Spectra of Charge-Transfer Complexes in the Molten State

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Since Mulliken set forth the distinguished charge-transfer theory, a considerable amount of effort has been devoted to explaining the various interactions responsible for the actual charge-transfer complexes.[1,2] However, as previous investigations were interested in the interactions around room temperature for the sake of convenience, our knowledge of the complexes is necessarity confined to those in solution and, to lesser degree, those in the solid state.

In our previous papers, we overcame the experimental difficulties due primarily to the thermal instability of the complexes and succeeded in measuring the gaseous absorption spectra of typical TCNE complexes.[3,4] On the other hand, attempts to detect the liquid-phase complex have been completely lacking. The observation of the spectra in the molten state might be useful for the analysis of the liquid-phase structure.

Recently, we investigated the charge-transfer complexes in the molten state and, for the first time, succeeded in the optical detection of the fused complexes. The absorption spectra were derived from the diffuse reflection spectra. The measurements were made at temperatures considerabley higher than the melting points, using a Beckman DK-2A spectroreflectometer.

We first prepared the *N,N*-dimethylaniline-*s*-trinitrobenzene 1 : 1 complex from an *N,N*-dimethylaniline solution of *s*-trinitrobenzene. The observation in the liquid phase was made at 150°C, which is higher by 50°C than the melting point of the complex. Figure 1 shows the liquid-phase absorption specrtum of the *N,N*-dimethylaniline-*s*-trinitrobenzene complex. The spectra in the solid state and in the *n*-heptane solution are added for the sake of comparison. In the solid, two characteristic charge-transfer bands were observed at 19300 and at 23300 cm^{-1}. However, the second band was missing in the other phases. The absorption maximum in the molten state was found at 21100 cm^{-1}, which corresponds to a blue shift of 1800 cm^{-1} from that found in the crystal. On the other hand, it was located at 21400 cm^{-1} in the *n*-heptane solution. It can be easily seen therein that, though each band-width is somewhat different, the absorption bands in the liquid phase and in the solution are almost superimposed upon each other. The naphthalene-TCNE complex also has similar tendencies in the liquid-phase spectrum.

It is widely known that, in the crystal, the presence of nearby charge-transfer complexes markedly alters the properties of the isolated complex. The complexes generally from an ∞:∞ complex instead of distinct 1 : 1 complexes. Though we can expect such situations in the liquid phase, at least in view of the optical absorption, we can not characterize them in the spectra. However, this fact dose not preclude the possibility that interactions inducing such phenomena as the liquid-phase exciton and the quite high conductivity exist in the liquid-phase complexes.[5,6]

We are now continuing to examine other type of charge-transfer complexes in the molten state.

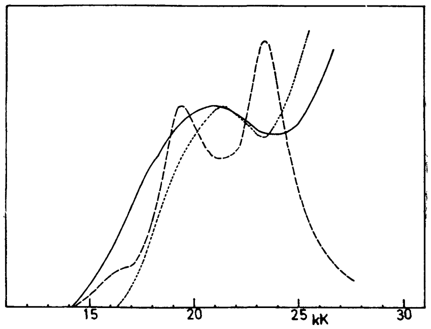

Fig. 1. Absorption spectra of the *N,N*-dimethylaniline-*s*-trinitrobenzene complex in various phases.
—— liquid-phase
------ *n*-heptane solution and
----- solid-state spectra

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