NOTES

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Polarization Dispersion in the Resonance Raman Spectra of EDA Complexes with TCNE and TCNB

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Synopsis. Polarization dispersion of the $\nu_{\mathrm{C\equiv N}}$ Raman line of the *N,N*-dimethylaniline-TCNB complex indicated that the two CT absorption bands are assignable to different acceptor orbitals, in contrast with those of TCNE complexes.

The resonance Raman effect (RRE) can be used to probe the nature of electronic excited states, and its faculty is fully exhibited by investigating the excitation profile and polarization dispersion. Charge transfer (CT) excited states of electron-donor-acceptor (EDA) complexes can suitably be investigated by RRE, as was demonstrated by Kaya *et al.*¹⁾ for the complexes of tetracyanoethylene (TCNE) with benzene homologues. They observed the RRE of $\nu_{\mathrm{C=C}}$ and $\nu_{\mathrm{C\equiv N}}$ of complexed TCNE by exciting radiations within the first CT absorption band, and concluded that some increase of equilibrium C=C and C≡N distances from the ground to CT excited states was responsible for the resonant intensity of those lines.

It has been known that two CT absorption bands appear in the complexes with strong electron acceptors such as chloranil and TCNE.²⁾ Those CT bands have been explained by the two CT configurations (illustrated in Fig. 1a) distinguished by the difference in electron-donating orbitals. On the other hand, Iwata *et al.*³⁾ showed that the two CT absorption bands observed for some complexes of 1,2,4,5-tetracyanobenzene (TCNB), though quite similar to the TCNE case, were more reasonably interpreted by another multi-CT scheme (shown in Fig. 1b) in which two CT configurations are distinct in the electron-accepting orbitals of TCNB. In order to investigate the validity of these multi-CT schemes further, the RRE has been measured for the *N,N*-dimethylaniline–TCNB complex and some TCNE complexes.

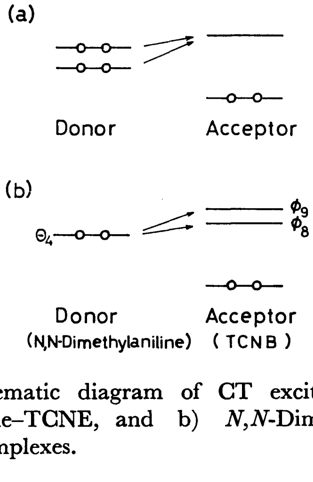

Fig. 1. Schematic diagram of CT excited states a) naphthalene–TCNE, and b) *N,N*-Dimethylaniline–TCNB complexes.

Experimental

Commercially obtained samples were used after appropriate purification, with the exception of TCNB, which was synthesized from pyromellitic acid and purified by sublimation. Raman spectra were recorded on JRS-S1 and JRS-400D spectrometers using exciting radiations from Ar⁺ (457.9⋯514.5 nm), Kr⁺(530.9, 568.2, 647.1 nm), and He–Ne (632.8 nm) lasers. The measurement was carried out on donor-excess solutions by using a rotating cell. The intensity and depolarization ratio were determined by checking with appropriate internal standards; these were solvent CH_2Cl_2 for TCNE and purposely added CCl_4 for TCNB.

Results and Discussion

Figure 2 shows the excitation profiles and polarization dispersions measured on $\nu_{\mathrm{C=C}}$ (1560 cm^{-1}) and $\nu_{\mathrm{C\equiv N}}$ (2230 cm^{-1}) of TCNE in the solution of naphthalene–TCNE complex. About 80% of TCNE is bound to form the complex²⁾ in the present donor-excess condition, so that the non-resonant intensity from free TCNE may be unimportant. The $\nu_{\mathrm{C\equiv N}}$ Raman band

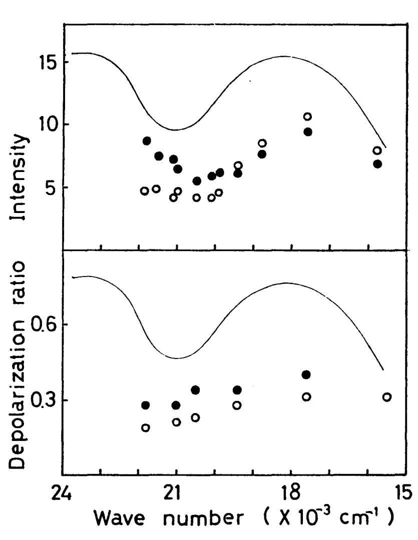

Fig. 2. Excitation profile and polarization dispersion of naphthalene–TCNE complex, naphthalene=0.1 mol/l, TCNE=0.005 mol/l in CH_2Cl_2 solution. (○): $\nu_{\mathrm{C=C}}$(1560 cm^{-1}), (●): $\nu_{\mathrm{C\equiv N}}$(2230 cm^{-1}), (——); absorption.

includes both A_g and B_{1g}** C≡N stretching modes. Since the ρ value is rather close to 1/3, which is the value expected for a Franck-Condon type resonance enhancement of the A_g mode, the depolarized B_{1g} intensity does not seem to be appreciably resonant in the CT band region. If the B_{1g} mode were resonant due to a vibronic coupling of the CT levels, the ρ plot should have shown generally higher values than that observed and tended upward at the high frequency side as in observed for the intensity plot. The slight dispersive trend of ρ observed for both $\nu_{C=C}$ and $\nu_{C\equiv N}$ may possible be caused by the interference of contributions from the first and second CT levels. Such an interference can take place because those CT transition moments may not be exactly parallel to each other on account of the mixing with locally excited states. Similar measurements have been carried out for the TCNE complexes of durene and pyrene, which also have two CT absorption bands in the visible; similar features of the depolarization ratio were found.

Figure 3 shows the results of the corresponding observations on *N*,*N*-dimethylaniline–TCNB complex.*** It is remarkable that the ρ ($\nu_{C\equiv N}$) increases towards the CT absorption maximum up to about 0.7 at a 514.5 nm excitation, while ρ ($\nu_{C=C}$) is kept nearly constant at about 1/3. This indicates that the depolarized $\nu_{C\equiv N}$ (B_{1g}) line is quite resonant in this system. The RRE intensity of a non-totally symmetric mode normally originates from vibronic coupling; thus, the above case may be most reasonably understood by the coupling of the first and second CT states illustrated in Fig. 1b, as will be descrived below. The contribution to a Raman tensor from a vibronic coupling of ψ_e and ψ_s states is proportional to the integral $\int \psi_e^*(\partial H/\partial Q_a)_0\, \psi_s d\tau$,[5] where Q_a is a normal coordinate. The integral can be reduced to a single electon one such as

$$\int \psi_e^*(H\partial/\partial Q_a)_0 \psi_s d\tau_1 \cdots d\tau_N = \int \upsilon^a(1)\rho_{es}(1)d\tau_1, \qquad (1)$$

where υ^a is the potential from a set of point dipoles produced by the nuclear displacement of mode a and ρ_{es} is the transition density defined by

$$\rho_{es}(1) = N\int \psi_e^*(1, \cdots, N)\psi_s(1, \cdots, N)d\tau_2 \cdots d\tau_N. \qquad (2)$$

Now, let us assume that the CT states of *N*,*N*-dimethylaniline–TCNB complex can be represented by

$$\psi_{CT1} = \Phi(\theta_4{}^{-1}\phi_8), \qquad \psi_{CT2} = \Phi(\theta_4{}^{-1}\phi_9), \qquad (3)$$

$$\Phi(\theta_4{}^{-1}\phi_k) = (1/\sqrt{2})[|\theta_1 \cdots \phi_4\overline{\phi}_k \cdots \overline{\phi}_7| + |\theta_1 \cdots \phi_k\overline{\theta}_4 \cdots \overline{\phi}_7|], \qquad (4)$$

where θ and ϕ represent the MO's of *N*,*N*-dimethylaniline and TCNB respectively, as shown in Fig. 1b. It is readily shown that

$$\rho_{CT1,CT2} = \phi_8\phi_9, \qquad (5)$$

which signifies that the transition density is spacially localized on the TCNB moiety. Then the significant coupling of the CT states (3) can take place only by the vibrational modes of the TCNB moiety, as is obvious from Eq. 1, providing that the mode a belongs to the same representation of TCNB symmetry (D_{2h}) as $\rho_{CT1,\,CT2}$ does. Since

$$\Gamma(\phi_8) \times \Gamma(\phi_9) = A_u \times B_{1u} = B_{1g},$$

the $\nu_{C\equiv N}$ (B_{1g}) mode meets the above requirement. On the other hand, it is obvious by a similar consideration that the transition density between the two CT configurations of Fig. 1a is one-sided on the donor molecule, so that the vibronic coupling by acceptor modes may be quite unlikely.

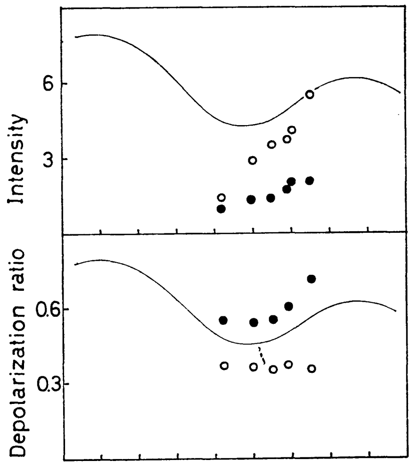

Fig. 3. Excitation profile and polarization dispersion of *N*,*N*-dimethylaniline–TCNB complex, TCNB=0.007 mol/l in *N*,*N*-dimethylaniline solution. (○): $\nu_{C=C}$(1542 cm^{-1}), (●): $\nu_{C\equiv N}$(2240 cm^{-1}), (——): absorption.

On the basis of above discussion, the present RRE result may be thought of as further evidence for the multi-CT schemes of Figs. 1a and b proposed for TCNE and TCNB complexes.

References

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** Representation of the D_{2h} group of TCNE.

*** Several other donors tried at the same time were not suitable enough to allow significant observation, because of insufficient solubility, CT band locations remote from available laser lines, apparent interference from intense locally excited absorptions, *etc.*