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Resonance Raman Spectra of Tetracyanoethylene Anion Dimers

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The resonance Raman spectra of TCNE$^-$M$^+$ (M=Na, K, Rb, Cs) in MTHF solutions have been measured at 100 K by exciting radiations within the long wavelength absorption band characteristic of the dimer (TCNE$^-$)$_2$. Two remarkably resonant lines have been observed at about 180 cm^{-1} and 150 cm^{-1}, showing an obvious change of the relative intensity depending on the counter cation species. The resonance behavior definitely indicates that the stretching vibration of interradical bond is responsible for these lines. Formation of two different types of dimer salts has been proposed as the most probable interpretation of the observed spectral behaviors.

A number of aromatic radical ions have been known to form the dimers under appropriate conditions of temperature and concentration. The formation of dimers is manifested by the temperature dependence of ESR and electronic spectra, which have been quantitatively investigated in several systems to discuss the monomer-dimer equilibrium.[1–4] Recently we studied the vibrational spectra of the dimers of some Würster's cations[5] and of *p*-benzosemiquinone anion,[6] by taking advantage of the resonance Raman effect. The spectra were obtained by exciting radiations close to the new long wave absorption bands characteristic of the dimer formation. In each case, a new resonant Raman line was observed at a low frequency and was assigned to the stretching vibration of interradical bond of the dimer, because of its remarkable and exclusive resonance enhancement by the dimer's characteristic absorption.

Tetracyanoethylene radical anion(TCNE$^-$) has been shown to form the dimer at low temperatures.[7] Itoh[4] carried out quantitative investigations of the ESR and electronic spectra, from which he obtained the heat of dimer formation for several counter alkali metal ions and for varied solvent compositions. He also measured the electronic spectra of solid salts, noticing the spectral similarity between the room temperature solids and low temperature solutions. Hinkel *et al.*[8] measured the resonance Raman spectra of TCNE$^-$Na$^+$ and TCNE$^-$K$^+$ solid films by exciting radiations within the broad low frequency absorption band. They observed a very broad and intense Raman band at about 170 cm^{-1} with the features sensitive to the condition of sample deposition. Making reference to the behavior of overtone progression, they assigned the band to several librational lattice modes, by assuming mixed formation of different crystal structures with changeable composition.

In this paper, we present the resonance Raman spectra of TCNE$^-$ dimers observed in the low temperature solutions, and discuss the results in connection with the existing experimental data mentioned above.

Experimental

TCNE$^-$M$^+$ (M=Na, K, Rb, Cs) was prepared by contacting 2-methyltetrahydrofuran(MTHF) solution of TCNE with an alkali metal film in an evacuated manifold. The Raman spectra were recorded for the solution at 100±2 K, where the sample was still kept fluid, by cooling with a regulated flow of cold nitrogen gas in a vacuum cell. The condition of spectroscopic measurement was almost equal to the previous studies.[5,6]

Results and Discussion

The Raman spectra of about 3×10^{-3} mol dm^{-3} TCNE$^-$Rb$^+$ solution in MTHF at 100 K are shown in Fig. 1 for some Ar$^+$ laser exciting radiations. These laser lines are located on the higher frequency side within the long wave absorption band characteristic of the dimer, as shown in Fig. 2. As the laser wavelength approaches the absorption maximum at about 540 nm, new Raman lines emerge at 180 cm^{-1} and 150 cm^{-1} with remarkable resonance enhancement, both showing the depolarization ratio of about 0.35. No monomer lines have appreciable intensity in the same conditions.

The aspect of things is essentially similar to the previous observations on Würster's cations[5] and *p*-

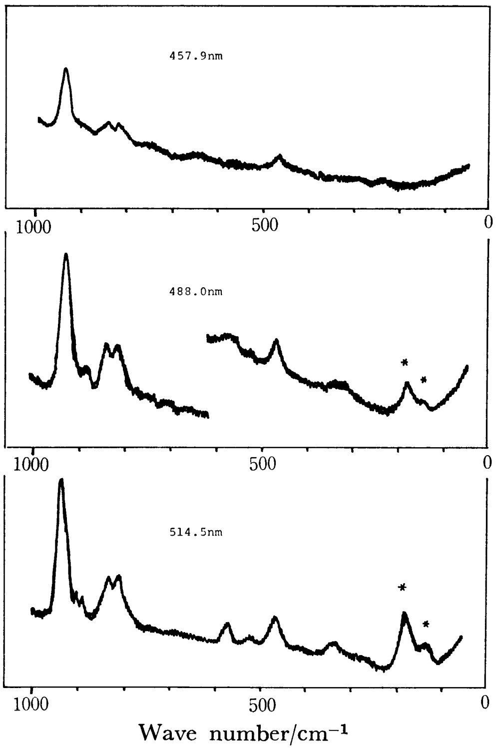

Fig. 1. Raman spectra of TCNE$^-$Rb$^+$ in MTHF solutions at 100±2 K. *Lines of the dimer.

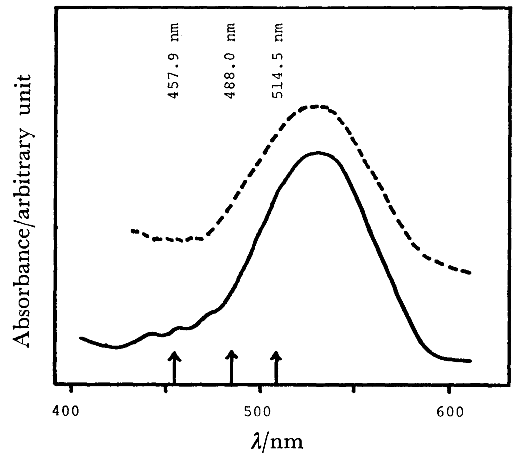

Fig. 2. Visible absorption spectra of $TCNE^-Na^+$ (solid line) and $TCNE^-Cs^+$ (broken line) in MTHF solutions at 100±2 K.

benzosemiquinone anion,[6] except that two well resolved new lines, instead of one, have been observed in the present spectra. Namely, it is little questionable that the 540 nm absorption band is attributed to the charge transfer type transition between $TCNE^-$ moieties of the dimer. The resonance Raman effect associated with this transition is most reasonably considered to originate in the Franck-Condon type term of the scattering tensor,[9] which is raised by the shift in the minimum position of interradical potential curves between the ground and excited states. Then, the strongly resonant low frequency lines obtained above are most likely associated with the stretching vibration of interradical bond. Here, we have tacitly assumed a parallel D_{2h} configuration of the dimer, by reason of the maximum overlap between the π-orbitals of both moieties. It may be noticed, however, that the electrostatic repulsion between the charge distributions on monomer ions is certainly against the D_{2h} structure, and the effect of attached counter cations brings further complexity.

Now, the appearance of two low frequency lines may possibly be due to the coupling of a low frequency dimer mode, composed of monomers' internal motion, with the strongly resonant interradical stretching mode. Such a coupling may be most probable for the symmetric combination of infrared active out-of-plane vibrations of monomers, and the Raman intensity of coupled modes is brought from the incorporated interradical motion. However, by measuring the spectra of other alkali metal salts under the same conditions, it has been found out that the intensity ratio of those two Raman lines changes remarkably depending on the counter cation species, as shown in Fig. 3. If we assume the coupled mode scheme as above, the observed intensity behavior signifies that the mixing ratio of internal and interradical mode amplitudes changes considerably by cation species, necessarily being attended by the corresponding frequency changes.

In the observed spectra, the higher frequency line is almost unchanged in the maximum position for different counter cation species, while a slight shift can be noticed for the lower frequency one, as shown in Fig. 4. A simple mechanical consideration shows that such a frequency behavior is rather unlikely in the above coupling scheme, and, even if admitted, cannot possibly be consistent with the observed intensity trend.

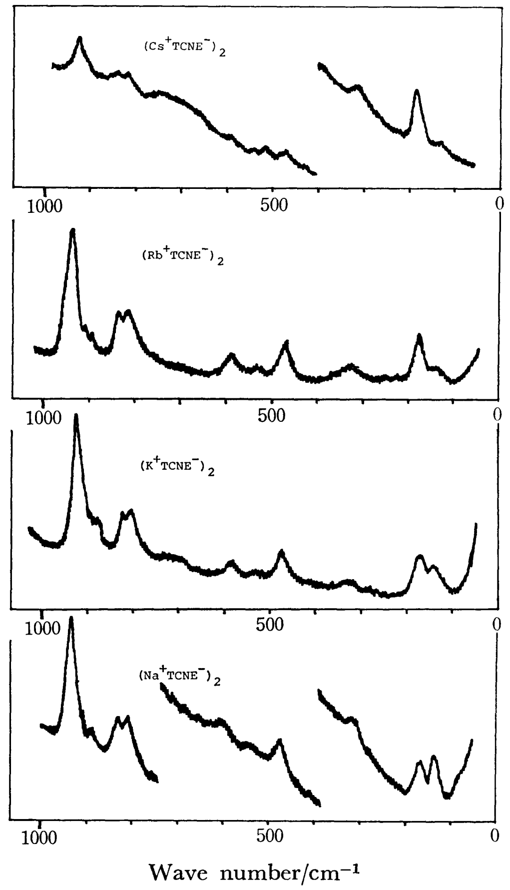

Fig. 3. Raman spectra of $TCNE^-M^+$ (M=Na, K, Rb, Cs) in MTHF solutions at 100±2 K with a 514.5 nm exciting radiation. The concentration is about 3×10^{-3} mol dm^{-3} for Na, K, and Rb salt and about 6×10^{-3} mol dm^{-3} for Cs salt.

There may arise another argument that the two Raman lines are assigned to separate interradical modes with different origins of electronic resonance, so that the relative intensity changes due to the gradual shift of resonance origins from Na to Cs salts. However, this does not seem probable either, because the resonant 540 nm absorption band is essentially unchanged for different counter cations as observed in Fig. 2, and also because the relative intensity of two Raman lines hardly changes by altering the exciting radiation from 514.5 nm to 488.0 nm. The scarce sensitivity of the dimer's characteristic absorption to the counter cation species may be realized by the fact that the associated transition, illustrated in Fig. 5, gives rise to no substantial change in charge distribution, unlike the other transitions between different monomer orbitals.

Thus, we are led to conclude that the dimer molecules are distributed in two different forms, so that the observed intensity change may be interpreted as due to the population change in those forms effected by replacing the counter cation. In view of the ordinary and unchangeable features of 540 nm absorp-

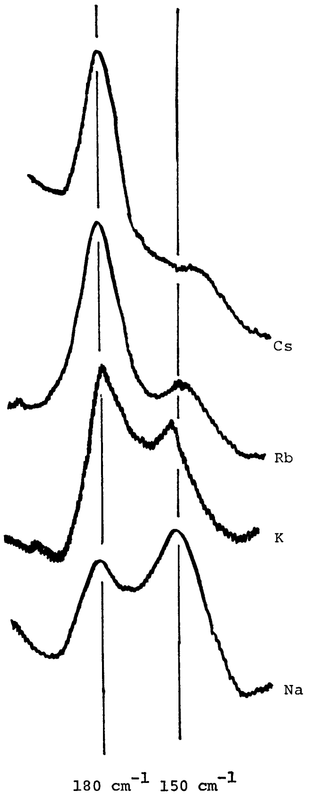

Fig. 4. Change of low frequency Raman features by counter cations in the spectra by 514.5 nm excitation.

tion band, the distinction between the two dimer forms may not consist in any notable difference in the interradical binding nature, but may be due to chemically less significant factors.

By investigating the temperature dependence of ESR and electronic absorption intensities, Itoh[4] showed that the heat of dimer formation($-\Delta H$) in MTHF solutions is appreciably dependent on counter cation species in the order $Na^+ > K^+ > Rb^+ > Cs^+$. He also showed that the $-\Delta H$ tends to be smaller for increasing solvation effect, from the same investigation by using THF/MTHF mixed solvents. The latter observation may be incorporated with the normally expected order of solvation strength, $Na^+ > K^+ > Rb^+ > Cs^+$, to suggest that the principal factor to give the above order of counter cation effect on $-\Delta H$ is not the solvation but more probably be ionic interactions. This is favorable for the supposition that two different modes of interaction between $(TCNE^-)_2$ and counter cations are responsible for the observed two Raman lines.

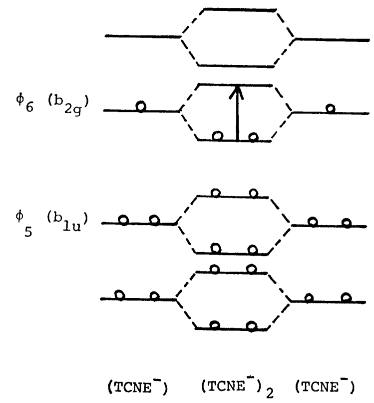

Fig. 5. MO scheme of $(TCNE^-)_2$ dimer formation. The arrow indicates the transition of 540 nm absorption.

Conceivable schemes may be the pair of $M^+(TCNE^-)_2M^+$ and $M^+(TCNE^-)_2//M^+$, where // represents intervening solvent molecules, or two different geometrical arrangements in $M^+(TCNE^-)_2M^+$, *etc.*, but further investigations are required for discussing those schemes significantly.

On the other hand, it may be noticed that the observed low frequency Raman lines are in good correspondence to those of solid salts[8] in the frequencies and resonant behavior. Accordingly, it seems fairly probable that the solid lines have essentially the same origin as the present solution lines rather than the librational modes in the previous assignment[8]. This observation gives support to the formerly given suggestion that the structure unit of the crystal is the dimer[4].

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