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RESONANCE RAMAN SPECTRA OF CHLORANIL ANION RADICAL DIMERS

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Two resonant lines were observed in the Raman spectra of chloranil anion radical dimers with exciting radiation close to the CT band, and were assigned to inter-radical stretching vibrations. The change of the relative intensity of these lines depending on counter ions was attributed to the formation of two different dimers.

Resonance Raman spectra characteristic of organic ion radical dimers have been obtained with exciting radiation close to the CT band. For example, a new broad resonant line was observed in the Raman spectra of p-phenylenediamine cation1) and p-benzosemiquinone anion2) radical dimers, and was assigned to an inter-radical stretching vibration. On the other hand, in tetracyanoethylene anion radical dimer $(\mathrm{TCNE}^{\overline{\cdot}})_2$, two resonant Raman lines, instead of one, were observed at 155 and 180 cm^{-1} showing obvious change of the relative intensity depending on the counter ions such as Na^+, K^+, Rb^+, and Cs^+.3) Formation of two different dimers was proposed as the most probable interpretation of the spectral behavior observed. We studied resonance Raman spectra of chloranil anion radical dimer, $(\mathrm{CA}^{\overline{\cdot}})_2$, in order to see whether this spectral behavior is observed in other dimers. It is well known that $\mathrm{CA}^{\overline{\cdot}}$ forms dimers in ethanol at low temperatures and a CT band appears at 670 nm.4)

Alkaline metal salts of chloranil (M·CA) were prepared by the method of Torrey and Hunter,5) where M is Li, Na, K, or Rb. The salt was dissolved in dry ethanol in vacuo; the concentration of this solution was ca. 10^{-3} mol/l. The solution was placed in an evacuated cylindrical Raman cell, and was cooled in a cryostat. Raman spectra were recorded on a JASCO R-800 spectrometer equipped with NEC GLG-108 He-Ne and GLG-3200 Ar^+ lasers.

Figure 1 shows the Raman spectra of Na·CA obtained with 632.8 nm excitation close to the CT band of the dimer. No Raman lines other than those of the solvent were observed in the spectrum at 200 K, because very few dimers are formed at this temperature and monomer lines are not resonance enhanced with this exciting radiation. When the solution was cooled to 140 K, seven new lines appeared. This spectral change was reversible and reproducible. On the other hand, none of these Raman lines were observed even at 140 K with 514.5 nm excitation far from the CT band. Therefore, these Raman lines are undoubtedly resonance enhanced by the CT transition of the dimer. Broad Raman lines at 114 and 168 cm^{-1} will be assigned to inter-radical stretching vibrations by comparison with those observed in the other dimers.1-3) The relative intensity of the former to the latter was dependent on the counter ions in the order $\mathrm{Li}^+ > \mathrm{Na}^+ > \mathrm{K}^+ > \mathrm{Rb}^+$. This is the same spectral behavior as observed in $(\mathrm{TCNE}^{\overline{\cdot}})_2$.

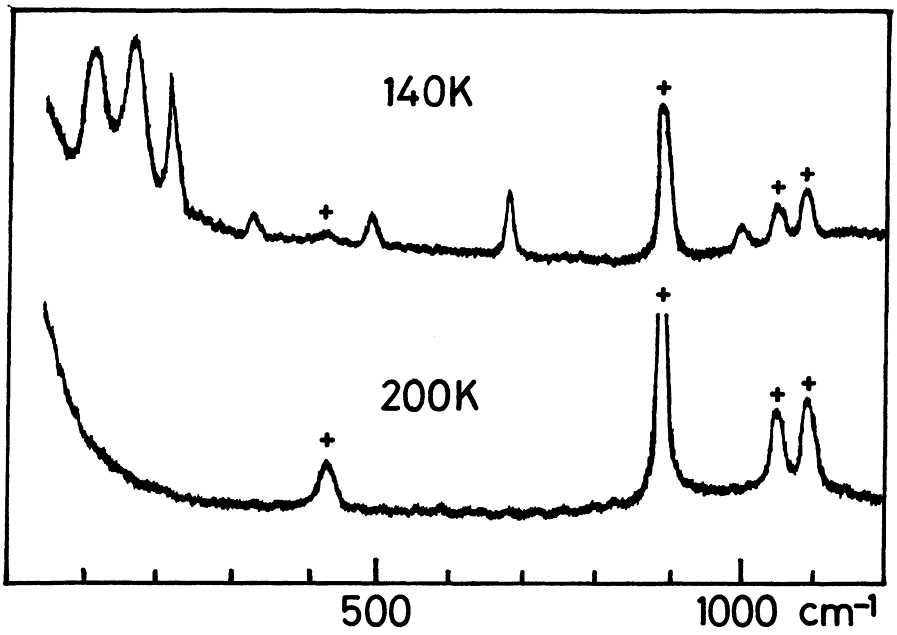

Fig.1 Resonance Raman spectra of Na·CA in ethanol at 200 K and 140 K with 632.8 nm excitation; ✚ Raman lines of the solvent.

It seems to be probable from this behavior that two different dimers are present in the solution and the ratio of the equilibrium concentrations of the dimers is dependent on the counter ions. This difference in the structure of these dimers is probably related to that in the pairing mode of the dimer and the counter ion, e.g., contact ion pairs and solvent separated ion pairs, although the details of these structures are not obtained at the present time.

The remaining five Raman lines at higher frequencies will be attributable to intra-radical vibrations of $CA^{\bar{\cdot}}$ moiety of the dimer. We tentatively assigned these lines by comparison of their frequencies with those of the monomer as follows. The lines at 217 and 683 cm^{-1}, and 335, 493 and 1000 cm^{-1} correspond to ungerade out-of-plane (220 and 695 cm^{-1}) and totally symmetric in-plane (334, 501, and 1016 cm^{-1}) vibrations of $CA^{\bar{\cdot}}$ respectively.6)

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