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Resonance Raman Spectra and Inter-radical Vibrations of Chloranil Anion Radical Dimers

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Resonance Raman spectra of chloranil anion radical dimers were measured in ethanol at 140 K by an exciting radiation within the CT band, and all the Raman lines observed were shown to be totally symmetric. Two strong Raman lines at 114 $\mathrm{cm^{-1}}$ and 168 $\mathrm{cm^{-1}}$ have been assigned to inter-radical stretching vibrations of the dimer. The relative intensity of these lines changed depending on the counter ion species. Formation of two dimers has been supposed to explain the spectral behavior. Influence of 18-crown-6 on the spectra was investigated. The result strongly suggests that one dimer gives two inter-radical Raman lines. Two interpretations are proposed for the simultaneous resonance enhancement of these Raman lines: mechanical coupling of the inter- and intra-radical vibrations or distorsion of the D_{2h} eclipsed dimer structure. Other five lines at higher frequencies have been assigned to intra-radical vibrations of the dimer.

A number of organic ion radicals are known to form dimers in the solution under appropriate conditions of temperature and concentration, and the monomer-dimer equilibrium has been studied by electronic absorption spectra.[1–3] Recently resonance Raman spectra of some ion radical dimers have been measured by exciting radiations close to the CT band, and new broad Raman lines have been observed at lower frequencies.[4–6] The Raman lines are assigned to the stretching vibrations of the inter-radical bond of the dimer because of the remarkable resonance enhancement by the CT transition of the dimer. In the case of tetracyanoethylene anion radical dimer, $(\mathrm{TCNE}^{\overline{\cdot}})_2$, in 2-methyltetrahydrofuran (MTHF),[6] two inter-radical Raman lines were observed at *ca.* 150 $\mathrm{cm^{-1}}$ and 180 $\mathrm{cm^{-1}}$, which showed obvious change of the relative intensity depending on the counter ions ($\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Rb^+}$, and $\mathrm{Cs^+}$). Formation of two different dimers has been proposed as the most probable interpretation of the spectral behavior.

Structure of organic ion radicals in the solution has been investigated by ESR spectra, but the dimer has the singlet ground state so that no ESR signals are observed. Electronic spectra have also given little information about the detailed structure of the dimer because the absorption bands are broad and structureless. Vibrational spectroscopy will be, at present, the most suitable tool for the structural investigation of the dimer in the solution. Resonance Raman spectra particularly have the advantage that the inter-radical vibrations are observed directly. The spectra will give information about the structure of the ground state as well as the excited state when the nature of the resonance Raman effect in the dimer is elucidated by accumulation of the data.

In this paper, we present the resonance Raman spectra of chloranil anion radical dimer, $(\mathrm{CA}^{\overline{\cdot}})_2$, in ethanol and discuss the result from the standpoint of the dimer structure.

Experimental

Commercially available chloranil (CA) was crystallized twice from dry benzene and sublimed twice *in vacuo*. Commercially available alkaline iodide (M·I) was dried *in vacuo* at 110 °C for 12 h to avoid the decomposition of radicals by moisture in the salts. Alkaline metal salts of chloranil (M·CA) were prepared from CA and M·I by the method of Torrey and Hunter in dry acetone or acetonitrile:[7] M= Li, Na, K, Rb, and Cs. It is well known that M·CA usually contains the solvent in preparation.[8] The salts, therefore, were dried over $\mathrm{P_2O_5}$ in an evacuated desiccator for a week. IR spectra of the salts agreed well with those reported in the literature.[9] The salt was dissolved in dry ethanol of spectroscopic grade *in vacuo* to give the sample solution (*ca.* 10^{-3} mol/dm^3).

A glass cryostat with quartz windows was used for both Raman and electronic absorption measurements. The cryostat was cooled by flowing cold $\mathrm{N_2}$ gas. Raman spectra were recorded on a JASCO R-800 Raman spectrometer equipped with a NEC GLG-108 He–Ne laser and GLG-3200 $\mathrm{Ar^+}$ laser. Electronic spectra were recorded on a Hitachi 200-20 spectrophotometer.

Results and Discussion

Observed Spectra. In the visible spectra of Na·CA (Fig. 1), only an absorption band of $\mathrm{CA}^{\overline{\cdot}}$ is observed at room temperature, but another new peak appears at 670 nm when the solution is cooled to 140 K. This peak is assigned to the CT band of $(\mathrm{CA}^{\overline{\cdot}})_2$.[3]

Time-dependence of the Raman spectra observed at room temperature showed that $\mathrm{CA}^{\overline{\cdot}}$ in ethanol was gradually decomposed even in oxgen-free atmosphere. The spectra of the monomer, therefore, were measured at 200 K because the radical was practically

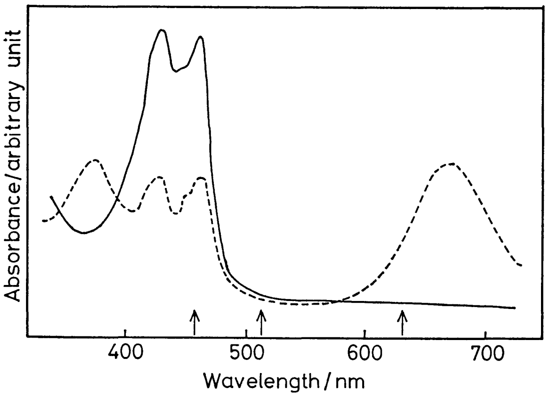

Fig. 1. Electronic absorption spectra of Na·CA in ethanol.
——: Room temperature, ----: 140 K.

stable and the dimer formation was still negligible at this temperature. Several Raman lines of $\mathrm{CA}^{\overline{\cdot}}$ were observed with 457.9 nm excitation within the first absorption band of the radical. The frequencies are given in Table 1 together with the frequencies and assignment reported by Girlando, *et al.*9) The table shows that the frequency of ν_1 in ethanol differs remarkably from that in acetone and in the powder sample.10) This mode is C=O stretching, and the difference probably arises from the hydrogen bond formation between the radical and the solvent.

Figure 2 shows the temperature-dependence of the Raman spectra of Na·CA by 632.8 nm excitation within the CT band of the dimer. No Raman lines of the sample are observed at 200 K because very few dimers are formed at this temperature and the monomer Raman lines show no practical resonance enhancement by this exciting radiation. When the solution is cooled to 140 K, seven new lines appear.11) This spectral change is reversible and reproducible. None of these Raman lines, on the other hand, are observed at 140 K when excited with the Ar^+ 514.5 nm line which is far from the CT band. These Raman lines, therefore, are undoubtedly resonance enhanced by the CT transition of the dimer. All of them were found to be totally symmetric by the depolarization ratios (*ca.* 1/3). The result shows that the resonance enhancement originates from the Franck-Condon type term of the scattering tensor.12) The Raman frequencies of the dimer are given in Table 2 together with the corresponding frequencies of the monomer. Raman lines at 114 cm^{-1} and 168 cm^{-1} are much broader than those at higher frequencies and will be assigned to inter-radical vibrations by comparison with those observed in other dimers.4–6) The relative intensity of 114 cm^{-1} line to 168 cm^{-1} line is dependent on the counter ions in the order, $\mathrm{Li}^+ \simeq \mathrm{Na}^+ > \mathrm{K}^+ > \mathrm{Rb}^+$ (Fig. 3).13) The result shows that a kind of association of the dimer and the cations is present in ethanol because it is not expected that the spectra of free dimers are affected by the counter ion. Ethanol has a large dielectric constant, so that the association should be very weak. The spectral change is similar to that observed in $(\mathrm{TCNE}^{\overline{\cdot}})_2$ in MTHF6) except that the magnitude of the change is rather small in the present case. Therefore, in the preliminary report of the present investigation,14) we gave the same interpretation as the case of $(\mathrm{TCNE}^{\overline{\cdot}})_2$; *i.e.*, two different

Table 1. Raman frequency of chloranil anion radical a)

Acetone solution b) ν/cm^{-1}	Ethanol solution c) ν/cm^{-1}	Assignment b)
334 s	335 m	$a_g\ \nu_5$
501 d)	512 s	$a_g\ \nu_4$
	846 w	$a_g\ \nu_4+\nu_5$
1016 w	1026 w	$a_g\ \nu_3$
1521 m	1562 m	$a_g\ \nu_1$
1584 m	1585 vs	$a_g\ \nu_2$

a) 457.9 nm excitation. b) Ref. 9 in the text. c) This work. d) Solution in dimethyl sulfoxide. See Ref. 9.

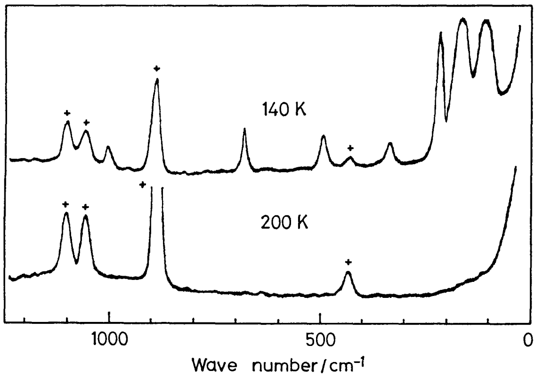

Fig. 2. Resonance Raman spectra of Na·CA in ethanol with 632.8 nm excitation.
+: Solvent Raman lines.

Table 2. Raman frequency of chloranil anion radical dimer

Observed dimer line a)			Corresponding monomer vibration	
ν/cm^{-1}	Assignment b)		ν/cm^{-1}	Assignment c)
114 s	a_g	R-R stretch. d)		
168 s	a_g	R-R stretch.		
217 s	a_g	Intra-radical vibration	220 e)	$b_{3u}\ \nu_{29}$
335 w	a_g		335	$a_g\ \nu_5$
493 m	a_g		512	$a_g\ \nu_4$
683 m	a_g		695 e)	$b_{3u}\ \nu_{28}$
1000 w	a_g		1026	$a_g\ \nu_3$

a) 632.8 nm excitation. b) This work. c) Ref. 9 in the text. d) R-R stretch. represents inter-radical stretching vibration. e) IR frequency of the solid radical salt. From Ref. 9.

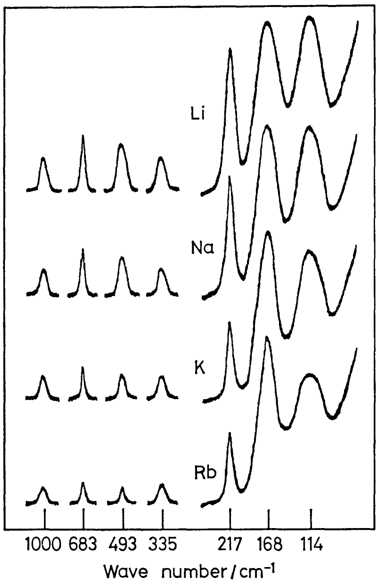

Fig. 3. Counter ion dependence of the resonance Raman spectra of $(\mathrm{CA}^{\overline{\cdot}})_2$ in ethanol.
Raman intensities of the dimers are normalized by that of 168 cm^{-1} line.

dimers were present in the solution and the ratio of the equilibrium concentrations was dependent on the counter ions. If this is the case, it is most probable that the difference in the dimers arises from that in the pairing mode of the dimer and the counter ion, *i.e.*, solvent-separated ion pairs and free ions: contact ion pairs are probably excluded because of the large dielectric constant of ethanol. It was also implicitly assumed in the report that the respective Raman lines corresponded to the same inter-radical vibrational mode of the different dimers. However, the large frequency difference ($>50\ \mathrm{cm}^{-1}$) in the two Raman lines seems to be unexplainable from this standpoint because the structures of the free dimer and the loosely ion-paired dimer are not expected to be so different from one another. Furthermore, strength of the association between the component cation and anion in the ion-paired dimers probably decreases continuously to the state of the free dimer in such a polar solvent as ethanol, and the dimers are not expected to be present as two distinct species. It is, therefore, necessary to examine the possibility that one dimer gives two inter-radical Raman lines.

For the purpose of this examination, spectral change by the addition of crown ether (18-crown-6) was investigated for K·CA in ethanol. It is well known that the crown ether forms very stable complexes with K^+; therefore, practically all of the cations are expected to be complexed by the crown ether. It has been reported that crown ethers inhibit the dimer formation of K·TCNE in MTHF, where ion pair formation is indicated by ESR.[15] Also in the present case, crown ether was expected to affect strongly the Raman spectra if the solution contained the ion-paired dimers of distinct structures. However, no drastic changes were observed when 18-crown-6 was added in large excess, but only a minor change occurred in the relative intensity of the two Raman lines (Fig. 4). The resulting spectrum is quite similar to that of Li·CA which is expected to have the strongest tendency to give free dimers because of the largest solvation energy of Li^+ among all the alkali metal cations. The change occurred probably because the crown ether weakened the interaction between the component cation and anion of the ion-paired dimer and allowed the dimer to be in the state of practically free dimers: this is also supported by the fact that the solubility of K·CA considerably increased by addition of the crown ether. The result shows that both of the two Raman lines are attributable to one dimer, *i.e.*, they correspond to the different vibrational modes of the dimer: mechanism of the simultaneous resonance enhancement of two inter-radical Raman lines will be discussed in the next section. The spectral change by the counter ion or the crown ether will be interpreted as follows. Observed Raman spectra correspond to the statistical average over the many dimers of various interaction strengths between the component cation and anion. If the average deviates by the counter ion or the crown ether and if the relative intensity of the Raman lines is different from each other in the respective dimers, spectral changes probably occur as observed in this investigation. Temperature dependences of the spectra were investigated in the range, 140 K—160 K, but practically no dependences were observed. The result may also be an evidence against the assumption of the presence of two dimers because the equilibrium of the dimers should be dependent on the temperature.

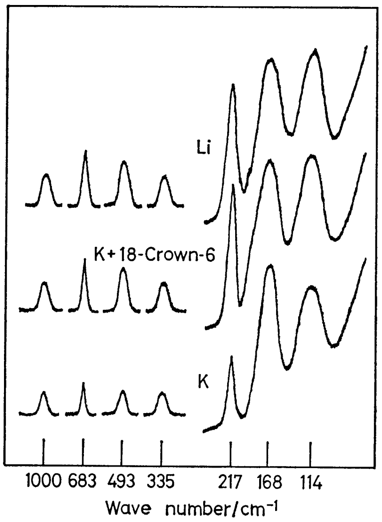

Fig. 4. Spectral change of K·CA by addition of 18-crown-6.

Normal Vibrations and Resonance Raman Effect. When two N-atomic radicals form a dimer, six of the 12 translational and rotational degrees of freedom of the radicals are frozen to produce six inter-radical vibrations of the dimer, because the resulting dimer only possesses six translational and rotational degrees of freedom. The inter-radical vibrational modes are easily obtained for the case of dimers of D_{2h} eclipsed structure by the *out-of-phase* combination of the corresponding translational and rotational motions of the component radicals: *e.g.*, the combination of the rotational motions around y-axis gives a librational mode of b_{1u} symmetry. The normal vibrations thus obtained are shown in Fig. 5: Q_1 (a_g), out-of-plane stretching mode; Q_2 (b_{1g}) and Q_3 (b_{2g}), in-plane slipping modes; Q_4 (a_u), in-plane twisting mode; Q_5 (b_{1u}) and Q_6 (b_{2u}), out-of-plane librational modes. The totally symmetric stretching mode, Q_1, is expected to show remarkable resonance enhancement by the Franck-Condon type term of the scattering tensor,[12] because the potential curves along this normal coordinate are probably much different from one another in the ground and CT excited states: the dimer is stabilized by the CT interaction in the ground state whereas in the CT excited state the component radicals should merely contact with each other in the solvent cage.[16] The two low frequency Raman lines will be assigned to this normal mode, but there is one totally symmetric vibration in the case of the eclipsed dimer structure. Two interpretations are possible for the simultaneous resonance enhancement of the two inter-radical Raman lines as discussed in the following.

The first interpretation is given on the basis of the intensity borrowing by the mechanical coupling of

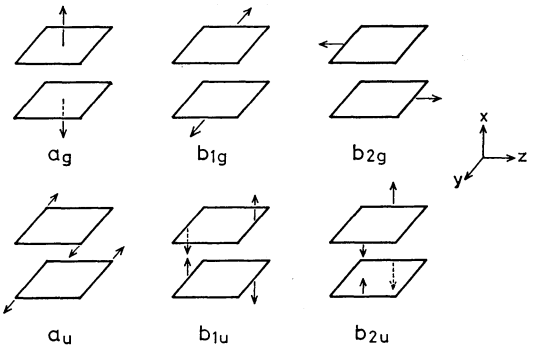

Fig. 5. Inter-radical vibrations of dimer of D_{2h} eclipsed structure.
Rectangles represent planer radicals, and arrows show the displacements: y- and z-axes are parallel to the molecular short and long axes respectively, and x-axis is perpendicular to the molecular plane.

the inter- and intra-radical vibrations. The number of the normal vibrations of the N-atomic radical is 3N−6, so that the resulting dimer possesses 2(3N−6) intra-radical vibrations. The *i*-th normal coordinates (Q_A^i and Q_B^i) of radicals A and B are combined with one another to produce new normal coordinates ($Q_\pm^i$): $Q_\pm^i=(1/\sqrt{2})(Q_A^i\pm Q_B^i)$. The combination gives totally symmetric vibrations only for the following two cases. When Q_A^i and Q_B^i are a_g modes, the *in-phase* combination (Q_+^i) remains totally symmetric and *out-of-phase* combination (Q_-^i) gives an IR-active mode of b_{3u} symmetry.[17] Q_+^i may couple with Q_1, but such a coupling is expected to be small because the former is the in-plane vibration whereas the latter is the out-of-plane one. When Q_A^i and Q_B^i are out-of-plane bending modes of b_{3u} symmetry, on the other hand, the *out-of-phase* combination gives totally symmetric vibrations. Such out-of-plane a_g modes are expected to couple considerably with Q_1 and to show resonance enhancement through the intensity borrowing by the mechanical coupling. Chloranil has three b_{3u} modes (ν_{28}, ν_{29}, and ν_{30}),[9] and the frequencies of ν_{28} and ν_{29} have been reported to be 695 cm^{-1} and 220 cm^{-1} respectively. The Raman lines at 683 cm^{-1} and 217 cm^{-1} will be reasonably assigned to the *out-of-phase* combination modes of ν_{28} and ν_{29} respectively. The third b_{3u} mode, ν_{30}, has not yet been observed for $\mathrm{CA}^{\dot{-}}$, but the frequency of the neutral molecule has been reported to be 88 cm^{-1}.[9] This mode may, therefore, have a frequency around 100 cm^{-1} also in the case of the radical. If Q_1 and the *out-of-phase* combination mode of ν_{30} strongly couple with each other, two Raman lines of comparable intensities will be observed in the low frequency region as in the present case. It is well known that, in general, the extent of the mechanical coupling of vibrational modes increases with a decrease in the difference of their frequencies. It is, therefore, expected that Raman line at 217 cm^{-1} has stronger intensity than that at 685 cm^{-1}: this expectation agrees well with the result obtained (Fig. 3).

The second interpretation is given on the basis of the distorsion of the dimer from the D_{2h} eclipsed structure. If the component radicals slip along y- or z-axis, the dimer has the slipped structure of C_{2h} symmetry; therefore, the dimer has two totally symmetric inter-radical modes. The slipped structure is occasionally met in the crystal structure of organic ion radical salts,[18] and the dimer in the solution may possess this structure. At this stage, it is not clear which interpretation is valid. The experiment of isotopic shifts may give conclusive information but $(\mathrm{CA}^{\dot{-}})_2$ seems to be unsuitable for this purpose because the inter-radical Raman lines are broad and the molecular weight is heavy: TCNE is a probable candidate for the purpose.

The remaining three Raman lines at 1000 cm^{-1}, 493 cm^{-1}, and 335 cm^{-1} will be assigned to ν_3, ν_4, and ν_5, respectively, as shown in Table 2. The mechanism for the resonance enhancement of these lines is not elucidated at present: measurements of the excitation profile may give some information. No distinct features have been observed in the region of ν_1 and ν_2. This result is probably attributed to the low sensitivity of our instrument in this region.

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