Raman Spectra of Alkali Metal Oxalates in Aqueous Solution. Evidence for Ion-pair Formation

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Laser Raman spectra of aqueous solutions of lithium, potassium, and caesium oxalates have been obtained; their band contours were examined by curve analysis. The intensities of several bands show distinct concentration and cation dependences. This behavior is connected with the ion-pair formation of oxalate ions with alkali metal cations. The assignments of C⩵O stretching vibrations are also discussed.

Laser Raman spectroscopy has been widely used to explore the properties of ion-pairs formed in aqueous solutions of electrolytes. For the Raman spectra of aqueous solutions of metal sulfates or nitrates, many authors¹⁾ have reported some additional bands which can give direct information on the ion-pairing. However, vibrational spectroscopic evidence for ion-pairing of carboxylate ions with metal cations is rarely found in earlier works, although thermodynamic evidence is presented by several authors.²⁾

The oxalate ion has the simplest structure among the dicarboxylate ions. This anion is expected to have a comparatively large association constant owing to the formation of a chelate-like structure with metal cations in aqueous solutions.

The Raman spectra of aqueous oxalate solutions were studied by several authors in order to assign the symmetry of the free oxalate ion. Murata and one of us (K.K)³⁾ assumed that the oxalate ion had a planar D_{2h} symmetry because of the inconsistency between the IR and Raman frequencies for the potassium salt. The same symmetry was also assumed by Ito and Bernstein⁴⁾ for the ion, while a staggered form of D_{2d} symmetry was proposed by Begun and Fletcher⁵⁾ and Bardet and Fleury⁶⁾ on the basis of the aqueous IR and Raman spectra. Schmelz, Miyazawa, Mizushima, Lane, and Quagliano⁷⁾ assumed the ion to have a D_2 symmetry by comparing the infrared data of the solid salt with the Raman data of an aqueous solution reported by Edsall.⁸⁾

In the present work Raman spectra of aqueous alkali metal oxalate solutions are interpreted in terms of coexistence of the free and the ion-paired oxalate ions. The assignment for the Raman bands of the free oxalate ion is also reexamined.

Experimental

The $Li_2C_2O_4$ and $K_2C_2O_4 \cdot H_2O$ used were reagent grade chemicals. $Cs_2C_2O_4$ was prepared by the reaction of Cs_2CO_3 with $H_2C_2O_4$; the crude product was purified by recrystallization. Aqueous solutions were prepared by dissolving a determined amount of these oxalates in distilled water. The solution were filtered through sintered glass filters prior to measurements of Raman spectra.

The Raman spectra were recorded on a JASCO Laser-Raman spectrometer (model R-800) using an Ar^+ ion (514.5 nm) laser as a excitation source at room temperature (20±1 °C). The frequencies of observed bands are accurate within $\pm 2\ cm^{-1}$.

The band decomposition was carried out using the FACOM 230 computer at Toyama University Computer Center, with a Voight function⁹⁾ taken as the spectral distribution of a single band.

Results and Discussion

Polarized Raman spectra observed for a saturated solution of potassium oxalate are shown in Fig. 1. The isotropic spectrum in Fig. 1 is the same in general spectral features as that given previously by Begun and Fletcher,⁵⁾ except that two very weak polarized bands at 1750 and 1360 cm^{-1} were recognized in the present study. However, it was found that some of the observed bands have obvious asymmetries and some features show distinct dependence on stoichiometric concentration.

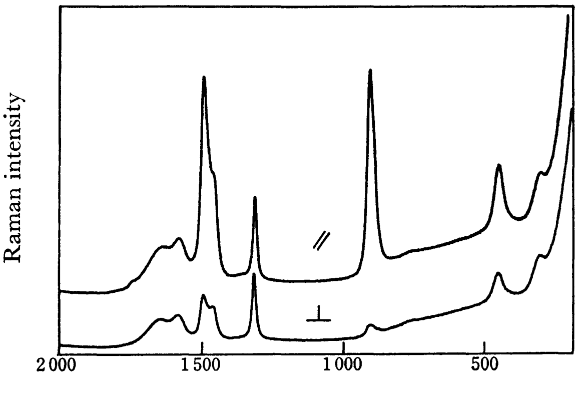


Fig. 1. Polarized Raman spectra of a satulated aqueous solution of potassium oxalate.

In previous works,³⁻⁷⁾ the band at *ca.* 900 cm^{-1} was assigned to the C–C stretching vibration as a single band. As shown by the solid line in Fig. 2, however, the isotropic and anisotropic band shapes observed for a saturated solution of potassium oxalate suggest that these bands consist of more than two components. We analyzed both the isotropic and anisotropic spectra, assuming that the components resolved in the isotropic spectrum are at the same frequencies as the corresponding ones in the anisotropic spectrum. As shown by broken lines in Fig. 2, both spectra can be resolved into three bands at 906, 891, and 872 cm^{-1}, of which the two high frequency bands are apparently polarized,

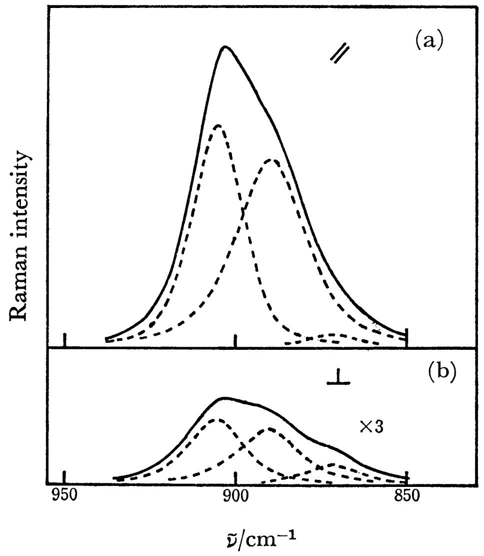


Fig. 2. The observed Raman contour (——) and the computer-analyzed components (-----) in C–C stretching region of a saturated aqueous potassium oxalate. (a) Isotropic spectrum; (b) anisotropic spectrum.

while the low frequency weak one is depolarized. This depolarized band is irrelevant to the discussion on the C–C stretching vibration and may be assigned to a combination band of the two IR frequencies[5] (525+351=876 cm^{-1}), because regardless of the symmetry of the oxalate ion the C–C stretching vibration belongs to a totally symmetric species and no band was observed near 872 cm^{-1} in the infrared spectra of either aqueous solution or solid state.[5] The Raman contours observed in this region for solutions of different concentrations of $K_2C_2O_4$ or for the $K_2C_2O_4$–KCl–H_2O solution were satisfactorily decomposed into the three bands, but the relative intensities of the two polarized bands showed a marked stoichiometric concentration dependence. Integrated intensity ratios of the 891 cm^{-1} band to the 906 cm^{-1} one for these systems are shown in Table 1. One notices from Table 1 that the ratio (I_{891}/I_{906}) increases with increasing stoichiometric concentration of potassium oxalate or by the addition of potassium chloride. From this behavior, the band at 891 cm^{-1} can be reasonably assigned to the C–C stretching vibration of ion-paired oxalate and the band at 906 cm^{-1} to that of the free oxalate ion.

TABLE 1. INTENSITY RATIOS OF THE 891TO 906 cm^{-1} BANDS[a)]

System	I_{891}/I_{906}
0.1 M $K_2C_2O_4$	0.44
0.5 M $K_2C_2O_4$	0.51
0.7 M $K_2C_2O_4$	0.54
1.0 M $K_2C_2O_4$	0.58
1.5 M $K_2C_2O_4$	0.63
1.8 M $K_2C_2O_4$	0.69
0.5 M $K_2C_2O_4$+2.5 M KCl	0.73
0.5 M $Li_2C_2O_4$	0.88
0.5 M $Cs_2C_2O_4$	0.48

a) The *ca.* 900 cm^{-1} contour has been assumed to consist of three bands whose widths are invariant for the different systems.

The Bjerrum theory[10)] on ion association suggests that, in the systems which contain a common ion, the smaller the radius of the counter ion is, the larger the association constant which can be expected. In order to examine the effect of metal cations on the ion-pair formation, the Raman spectrum of an aqueous solution of lithium or caesium oxalate was also observed. The Raman contours of the C–C stretching region of these systems were also resolved into three bands. The frequency shifts of these bands with the variation of cations were about ±3 cm^{-1}, and within the error estimated from both the measurements and the curve analysis. However, some cation dependence was found in the relative intensities of the two polarized bands. At the same stoichiometric concentration (0.5 M) the value of the I_{891}/I_{906} ratio, which is a measure of the degree of ion-pair formation, decreases in the order of lithium>potassium>caesium oxalate (see Table 1). This order also supports the above assignment of the C–C stretching region.

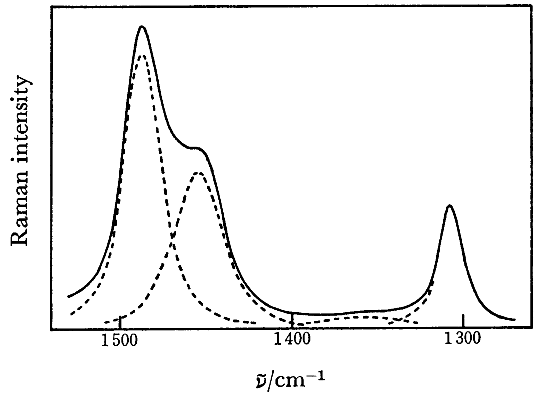


Fig. 3. The observed Raman contour (——) and the computer-analyzed components (-----) from 1270 to 1530 cm^{-1} of a saturated aqueous potassium oxalate.

The spectrum in the C=O stretching region for a saturated solution of potassium oxalate is shown in Fig. 3 (solid line). The resolution of the band contour into components is also shown in Fig. 3 (broken line). The resulting bands are situated at 1308, 1360, 1456, and 1488 cm^{-1}. The very weak and broad band at 1360 cm^{-1} is polarized and may be assigned to a combination band such as the C–C stretching and the CO_2^- bending modes (906+450=1356 cm^{-1}). The two bands at 1456 and 1488 cm^{-1} are clearly polarized, as is seen in Fig. 1. As shown in Table 2, there is some confusion in the assignments of the bands in this region, particularly of the band at 1456 cm^{-1}, depending on the symmetry of the free oxalate ion in the previous studies.[3–7)] The Raman contours from 1400 to 1550 cm^{-1} in various systems are shown in Fig. 4. The relative intensity of the 1456 cm^{-1} band distinctly depends on both the stoichiometric concentration of oxalate and the variation of cations, just as that of the 891 cm^{-1} band does.

Figure 5 shows integrated intensity ratios of the 1308, 1456, and 1488 cm^{-1} bands to the 906 or 891 cm^{-1}

TABLE 2. OBSERVED RAMAN FREQUENCIES (cm^{-1}) AND THEIR ASSIGNMENTS OF THE C=O STRETCHING REGION OF AQUEOUS POTASSIUM OXALATE AND OF THE SYMMETRY (POINT GROUP) OF THE FREE OXALATE ION

D_{2h}				D_{2d}				D_2		D_2 or D_{2d}	
M.K.[3]		I.B.[4]		B.F.[5]		B.F.[6]		S.M.M.L.Q.[7]		This work	
Obsd	Assign.	Obsd	Assign.[a]	Obsd	Assign.	Obsd	Assign.	Obsd[c]	Assign.	Obsd	Assign.
		1305	ν_8	1309	ν_7	1310	ν_7	1310	ν_{11}	1308	ν_{11} for D_2 or ν_5 for D_{2d}
1450		1452	$\nu_{10}+\nu_{11}$	1458[b]	$2\nu_8$	1456[b]	$2\nu_8$	1457		1456	ν_1 for ion-pair
1485	ν_1	1488	ν_1	1487	ν_1	1486	ν_1	1489	ν_1	1488	ν_1 for D_2 or D_{2d}
				1577[b]	ν_5	1581[b]	ν_5	1580		1575	ν_5 and ν_9 for D_2 or ν_7 for D_{2d}
1664	ν_5	1660	ν_5					1647			ν_5 for ion-pair

a) The numbering of the fundamentals is in accord with that of Schmelz *et al.*[7] b) These frequencies were interpreted to be a result of Fermi resonance. c) These data were obtained by Edsall.[8]

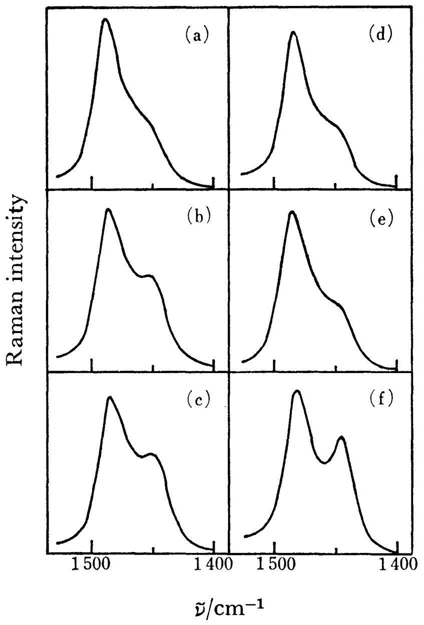


Fig. 4. The observed Raman bands from 1400 to 1500 cm^{-1} in various systems (a) 0.1 M $K_2C_2O_4$ (b) 1.8 M $K_2C_2O_4$ (c) 0.5 M $K_2C_2O_4$ +2.5 M KCl (d) 0.5 M $Cs_2C_2O_4$ (e) 0.5 M $K_2C_2O_4$ (f) 0.5 M $Li_2C_2O_4$.

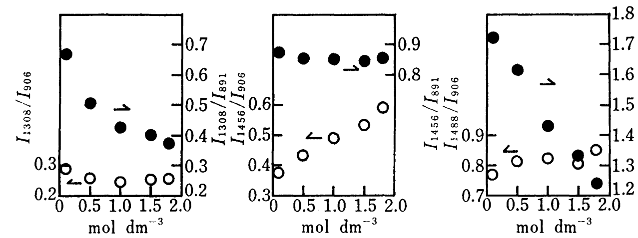
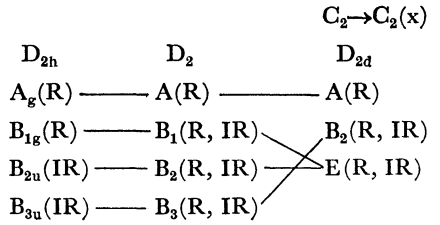


Fig. 5. Plots of the intensity ratios of C=O stretching bands to C–C stretching bands against the stoichiometric concentrations of potassium oxalate.

band *vs.* the stoichiometric concentration of potassium oxalate. Unfortunately, the integrated intensity of the band at 1575 cm^{-1} could not be obtained with enough accuracy for a quantitative discussion, because of its weakness and the overlapping with water bands. The independencies of the stoichiometric concentration are found for the intensity ratios of the 1308 and 1488 cm^{-1} bands to the 906 cm^{-1} band in Fig. 5. The same is true for the ratio of the 1456 cm^{-1} band to the 891 cm^{-1} band. The bands at 906, 1308, and 1488 cm^{-1} thus belong to the vibrations of the free oxalate, while the bands at 891 and 1456 cm^{-1} belong to those of the ion-paired oxalate.

Earlier studies on the vibrational spectrum of the oxalate ion were based mainly on the number of Raman active C=O stretching modes in the determination of the symmetry of the ion. The free oxalate ion in an aqueous solution should have one of three conformations: D_{2h} (planar), D_{2d} (two CO_2^- planes are at right angles), and D_2 (two CO_2^- planes are rotated with respect to each other by an angle which is not 90°). Symmetry correlations and vibrational activities related to the C=O stretchings are as follows.



An oxalate ion in solid $K_2C_2O_4 \cdot H_2O$ has a planar symmetry[11] and so the Raman and IR activities are mutually exclusive. Recently, Eriksson and Nielsen[12] found the Raman active antisymmetric and symmetric C=O stretching vibrations (A_g and B_{1g} modes) for polycrystalline and single crystal $K_2C_2O_4 \cdot H_2O$ at *ca.* 1600 and 1444 cm^{-1}, respectively. Two IR active stretching vibrations were observed for the salt at 1600 and 1310 cm^{-1} by Schmelz *et al.*[7] and at 1610 and 1312 cm^{-1} by Begun and Fletcher.[5] These vibrations were also examined in detail by Fukushima[13] in terms of the lattice vibrations of hydrated potassium oxalates. Schmelz *et al.*[7] have assigned the former to the antisymmetric vibration and the latter to the symmetric one. These assignments have been regarded as reasonable by the comparison of the frequencies with the Raman data,[12] though the opposite assignments had been given by Begun and Fletcher.[5] Cadene and Fournel[14] observed bands at *ca.* 1600 and *ca.* 1300 cm^{-1} in both the IR and Raman spectra of single crystal $(NH_4)_2C_2O_4 \cdot H_2O$, where the dihedral angle between two CO_2^- planes is 26.6°.[15] They have assigned the two bands to the antisymmetric and symmetric (not totally) C=O stretching vibrations, respectively, though their assignments were made on the basis of the D_{2d} symmetry for the oxalate ion. By comparing the two antisymmetric C=O stretching vibrational frequencies obtained in the previous studies,[5,7,12,14] little difference was found between the two vibrational frequencies for the ion whose symmetry is D_{2h} or D_2. There may be an accidental degeneracy in some cases. If the ion has a D_{2d} symmetry, the two antisymmetric C=O stretching frequencies are degenerate. For the structure of the free oxalate ion in aqueous solution, Begun and Flecher[5] pointed out that the ion has D_{2d} symmetry, because they found the existence of three coincidences between the IR and the Raman bands in the C=O stretching region of the spectra for aqueous solutions of alkali metal oxalates. Because of the appearance of the *ca.* 1300 cm^{-1} Raman band, which is reasonably assigned to the symmetric C=O stretching vibration, we conclude that the free ion does not have a planar structure. The assignment of the proper symmetry (D_2 or D_{2d}) of free oxalate, however, is difficult, because of the possibility of the accidental degeneracy in the two antisymmetric C=O stretching vibrations or the serious overlapping of several bands at *ca.* 1600 cm^{-1}. The tentative assignments of C=O stretchings are shown in Table 2.

The reason why only a Raman band which belongs to the C=O stretching vibrations has been detectable for the ion-paired oxalate may be discovered on the assumption that the oxalate ion has a planar and quasi-centrosymmetric structure. If the symmetry of the ion-paired oxalate is closer to D_{2h}, the intensity of the Raman band due to the symmetric vibration at *ca.* 1310 cm^{-1} will be less intense. This assumption may be supported by the low frequency shifts of the C–C stretching and the totally symmetric C=O stretching vibrations for ion-paired oxalate, compared with those for free oxalate in aqueous solutions; these vibrations were observed at 881 and 1444 cm^{-1} for polycrystalline $K_2C_2O_4 \cdot H_2O$.[12] Some planarity of ion-paired oxalate will be brought preferably by the formation of a chelate-like structure; because the interaction between oxalate and alkali metal ions will be mainly ionic, the oxalate ion is also expected to be kept in a quasi-centrosymmetric structure. Even if the interaction between cation and anion were covalent to some degree and thus the oxalate ion lost its quasi-centrosymmetric structure, the Raman band due to the (not totally) symmetric C=O stretching vibration would not be detectable in the range 1300—1400 cm^{-1}; this result is suggested by the fact that no Raman band was detected in the range 1300—1400 cm^{-1} for oxalato aluminium[16] or beryllium complex.[17] The Raman active antisymmetric C=O stretching vibrations for ion-paired oxalate will be expected at *ca.* 1600 cm^{-1}. Serious overlapping of the bands with the free oxalate or water bands will then occur. No useful information on band overlapping has yet been provided by Raman spectral measurements in D_2O, but the broad Raman band at 1575 cm^{-1} may reflect such a situation.

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