Monatshefte für Chemie 111, 1265—1272 (1980)

Monatshefte für Chemie

Raman and Infrared Spectra of $^{6}Li_2C_2O_4$ and $^{7}Li_2C_2O_4$

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(Received 21 February 1980. Accepted 27 March 1980)

Raman and infrared spectra of polycrystalline $^{6}Li_2C_2O_4$ and $^{7}Li_2C_2O_4$ have been investigated in the wavenumber region from 1,800 to 40 cm^{-1}. The internal $C_2O_4^{-2}$ vibrations have been studied on the basis of a D_{2h} molecular structure and the correlation field splittings have been found to be about 40 cm^{-1} for the stretching modes and about 15 cm^{-1} for the bending modes. The external vibrations of the Li^+ and $C_2O_4^{-2}$ sites have been discussed by considering the results of the factor group analysis and the $^{6}Li/^{7}Li$ isotope effect on the normal vibrations.

(Keywords: Correlation field band splitting; $^{6}Li/^{7}Li$ *isotope effect; Lithium oxalate; Raman and infrared spectral data)*

Raman- und Infrarot-Spektren von $^{6}Li_2C_2O_4$ *und* $^{7}Li_2C_2O_4$

Es wurden *Raman*- und IR-Spektren von polykristallinem $^{6}Li_2C_2O_4$ und $^{7}Li_2C_2O_4$ im Bereich der Wellenzahlen von 1800 bis 40 cm^{-1} untersucht. Die internen Schwingungen wurden auf der Basis einer D_{2h} Molekülstruktur analysiert. Für die Streckschwingungen wurde eine Korrelationsaufspaltung von etwa 40 cm^{-1} gefunden, für die Deformationsschwingungen etwa 15 cm^{-1}. Die Diskussion der externen Schwingungen von Li^+ und $C_2O_4^{-2}$ erfolgte unter Berücksichtigung der Resultate der Faktorgruppenanalyse und des $^{6}Li/^{7}Li$ Isotopeneffekts auf die Normalschwingungen.

Introduction

Recently the optically active normal vibrations of some inorganic lithium compounds have been investigated taking the results of the factor group analyses into consideration and the effectiveness of the $^{6}Li/^{7}Li$ isotope effect on the normal vibrations has been discussed to analyse the observed vibrational spectra[1–8]. The spectral data for solid state anhydrous dilithium oxalate, $Li_2C_2O_4$, have been reported by several authors[9–12], however the contents of these previous papers have been limited to the infrared active internal vibrations of the oxalate ion only and the *Raman* active ones have not yet been discussed up to the

0026-9247/80/0111/1265/$ 01.60

present. Also, the external vibrational modes of the Li^+ and $C_2O_4^{-2}$ sites and the correlation field band splittings of the internal $C_2O_4^{-2}$ vibrations have not been investigated as yet by any means of the vibrational spectroscopy.

In the present work, the *Raman* and infrared spectra for polycrystalline $^6Li_2C_2O_4$ and $^7Li_2C_2O_4$ are reported and the observed spectral data are analysed taking the results of the normal mode analysis for the monoclinic C_{2h}^5 space group, the $^6Li/^7Li$ isotopic wavenumber shifts and the correlation field band splittings of the internal $C_2O_4^{-2}$ vibrations into account.

Experimental

$^6Li_2C_2O_4$ and $^7Li_2C_2O_4$ were prepared, respectively, by neutralization of $^6LiOH \cdot H_2O$ and $^7LiOH \cdot H_2O$ with oxalic acid to *pH* 5.0-6.0. As the starting materials, $^6LiOH \cdot H_2O$ was converted from metallic ^6Li ($> 95\%$ enriched) by the reaction with water and lithium hydroxide monohydrate commercially obtained was used as $^7LiOH \cdot H_2O$ without further purification. The neutralized aqueous solution was evaporated slowly until $Li_2C_2O_4$ was crystallized and the precipitate was completely dried under reduced pressure. The purities of the reaction products were checked by the analysis for $C_2O_4^{-2}$ applying the ion-exchange technique and also by the atomic absorption spectrochemical analysis for Li^+.

The *Raman* spectra were recorded in the 1,800-40 cm^{-1} region for the polycrystalline samples using a Jarrell-Ash model 25-300 spectrometer. The 488.0 and 514.5 nm lines of an Ar^+ laser were used as the exciting source. The infrared spectra were also recorded in the 1,800-40 cm^{-1} region for Nujol and Fluorolube mulls between two CsI or polyethylene plates using a Perkin-Elmer IR 180 spectrophotometer. The spectral resolution in this study was typically 2.0-4.0 cm^{-1}, but a resolution of 5.0-8.0 cm^{-1} was used for broad bands. The observed bands should be accurate to ± 2.5 cm^{-1}.

Results and Discussion

According to the X-ray diffraction study by *Beagley* and *Small*[13], anhydrous dilithium oxalate crystallizes into a monoclinic lattice of space group $P2_1/n \equiv C_{2h}^5$ from aqueous solution and the crystallographic unit cell, which is also a primitive unit cell, contains two formula units of $Li_2C_2O_4$. In the crystal force field, the oxalate ions occupy sites of symmetry C_i located at positions $(0, 0, 0)$ and $(^1/_2, ^1/_2, ^1/_2)$, while four equivalent lithium ions are situated in general positions of symmetry C_1. The results of the factor group analysis for $Li_2C_2O_4$ are given in Table 1. The structure of the reduced representation of the 45 optically active normal modes of vibration is found to be

$$\Gamma_{vib} = 12\,A_g + 12\,B_g + 11\,A_u + 10\,B_u.$$

The normal vibrations of species A_g and B_g are active in the *Raman* spectrum, while those of species A_u and B_u are active in the infrared spectrum.

In Table 2, the *Raman* and infrared wavenumbers observed for polycrystalline $^6Li_2C_2O_4$ and $^7Li_2C_2O_4$ are summarized, together with the relative intensities. To facilitate the band assignment and discussion of the normal vibrations, the internal and external vibrations will be treated separately.

Table 1. *Result of factor group analysis for* $Li_2C_2O_4$

C_{2h}^5	N	n	R'	T'		T
		$C_2O_4^{-2}$	$C_2O_4^{-2}$	$C_2O_4^{-2}$	Li^+	
A_g	12	6	3	0	3	0
B_g	12	6	3	0	3	0
A_u	12	6	0	5		1
B_u	12	6	0	4		2

N, number of total freedom; n, number of internal vibrations; R', number of rotational lattice vibrations; T', number of translational lattice vibrations; T, number of translations.

Internal Vibrations

Since the oxalate ion in the $Li_2C_2O_4$ crystal has the C_i site symmetry, the molecular structure of the ion is found to be non-planar. However, it is also known from the X-ray structural analysis[13] that the deviations of the six atoms from an imaginary molecular plane are quite negligible. In addition, the C—O bond distances are found to be 1.264 and 1.252 Å and the C—C—O valence angles to be 116.4° and 116.3°. Therefore, it can be assumed that the free oxalate ion has the D_{2h} planar structure. A symmetry correlation diagram among the D_{2h} molecular group, the C_i site group and the C_{2h}^5 factor group is presented in Table 3, together with the numbering of normal vibrations. Since the shortest O···O distance between two different oxalate ions is 2.814 Å and somewhat shorter than twice the *van der Waals* radius of oxygen[14], the band separations of the internal vibrations due to the correlation field effects are expected to be not so small. The vibrational assignment is carried out taking the *Raman*-infrared mutual exclusion rules into account and in comparison with the vibrational analyses for $Na_2C_2O_4$ and $Na_2C_2O_4 \cdot H_2O_2$[15], $K_2C_2O_4 \cdot H_2O$[16–18] and $(NH_4)_2C_2O_4 \cdot H_2O$[19].

For the oxalate ion whose site symmetry is not far from D_{2h}, the C—O stretching vibrations are expected in the 1,670-1,580 cm^{-1} (ν_{11}), 1,650-1,570 cm^{-1} (ν_5), 1,490-1,440 cm^{-1} (ν_1) and 1,380-1,300 cm^{-1} (ν_9) regions[12, 15–18]. Taking the symmetries of the vibrational modes into account, two *Raman* intense bands at 1,647 and 1,487 cm^{-1} and two

Table 2. *Raman and infrared spectral data (in cm^{-1}) for* $^6Li_2C_2O_4$ *and* $^7Li_2C_2O_4$

$^6Li_2C_2O_4$		$^7Li_2C_2O_4$		Assignment	
Raman	Infrared	Raman	Infrared		
1744 w		1744 w		$2\nu_2$	
	1660 vs,br		1660 vs,br	ν_{11}	ν(C-O)
1647 m		1647 m		ν_5	ν(C-O)
1609 w		1609 w			
1487 vs,br		1487 vs,br		ν_1	ν(C-O)
	1420 w		1420 w	$\nu_2+\nu_{10}$	
	1392 w		1391 w		
	1375 w,sh		1373 w,sh	ν_9	ν(C-O)
	1336 vs		1336 vs		
909 s		909 s		ν_2	ν(C-C)
874 m		873 m			
	786 s,sh		784 s,sh	ν_{12}	$\rho(CO_2)$
	775 s		775 s		
612 w		611 w		ν_6	$\rho(CO_2)$
598 w		594 w			
	529 s,sh		528 s,sh	ν_{10}	$\delta(CO_2)$
	513 s		512 s		
513 m		511 m		ν_3	$\delta(CO_2)$
503 w,sh		501 w,sh			
468 w,br		437 w,br		T'(Li^+)	

Table 2 (continued)

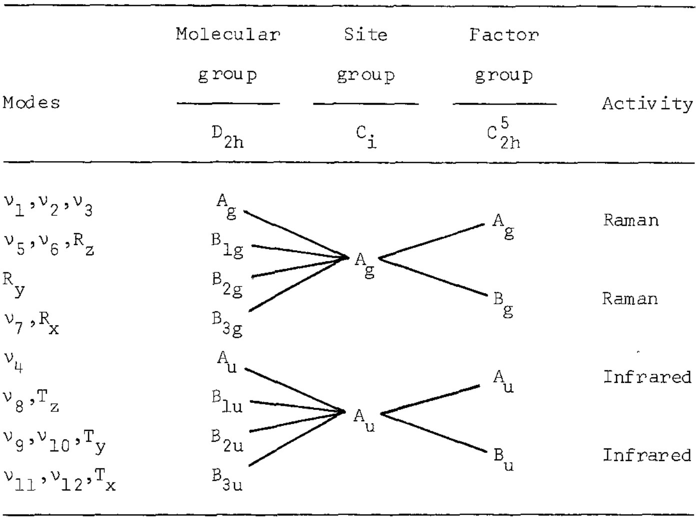
$^6Li_2C_2O_4$		$^7Li_2C_2O_4$		Assignment	
Raman	Infrared	Raman	Infrared		
	460 s,br		435 s,br	$T'(Li^+)$	
392 w		390 w		ν_7	$\omega(CO_2)$
387 vw,sh		386 vw,sh			
	375 s		374 s	ν_8	$\omega(CO_2)$
	358 m,sh		356 m,sh		
	290 m,br		285 m,br	ν_4	$\tau(C-C)$
230 w		227 w		$R'(C_2O_4^{-2})$	
	214 m		212 m	$T'(C_2O_4^{-2})$	
196 w		196 w		$R'(C_2O_4^{-2})$	
159 s		159 s		$R'(C_2O_4^{-2})$	
136 vs		136 vs		$R'(C_2O_4^{-2})$	
	116 s		116 s	$T'(C_2O_4^{-2})$	
97 vs		97 vs		$R'(C_2O_4^{-2})$	
	88 s		87 s	$T'(C_2O_4^{-2})$	
85 s		84 s		$R'(C_2O_4^{-2})$	

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

infrared intense bands at 1,660 and 1,336 cm^{-1} are directly assigned as ν_5, ν_1, ν_{11} and ν_9, respectively. The band splittings due to the correlation field effect are observed for ν_5 and ν_9 and the weak bands at 1,609 and 1,375 cm^{-1} of $^6Li_2C_2O_4$ and those at 1,609 and 1,373 cm^{-1} of $^7Li_2C_2O_4$ are also assigned to the C—O stretching vibrations. On the other hand, it is very difficult to find out the band splittings of ν_{11} and ν_1 because these split bands are covered with the very strong and broad bands at 1,660 and 1,487 cm^{-1}. The band separations of about 40 cm^{-1} are comparable with those for $Na_2C_2O_4$ and $Na_2C_2O_4 \cdot H_2O_2$[15], but these values are remarkably larger than those reported for $K_2C_2O_4 \cdot H_2O$[16–18]. The C—C stretching vibrations (ν_2) are identified at about 900 cm^{-1} with the correlation field effect of about 35 cm^{-1}. The fundamental wavenumbers of the C—C stretching vibrations are found to be not so affected by the structure changes of the oxalate ions in the crystals[15–19].

Since the oxalate ion in the $Li_2C_2O_4$ crystal has the C_i site symmetry, there are three *Raman* active and three infrared active CO_2 bending vibrations and each vibrational mode may be split by the correlation field. The fundamental bands of the CO_2 bending vibrations are expected in pairs in the wavenumber region from 800 to 250 cm^{-1} and, of course, these bands do not show the characteristic $^6Li/^7Li$ isotopic wavenumber shifts. Taking into account the band assignments of $Na_2C_2O_4$ and $Na_2C_2O_4 \cdot H_2O_2$[15], the *Raman* bands at about 600, 510 and 390 cm^{-1} are undoubtedly assigned to the CO_2 rocking (ν_6), scissoring (ν_3) and wagging (ν_7) vibrations. While, the infrared active CO_2 rocking (ν_{12}), scissoring (ν_{10}) and wagging (ν_8) vibrations are identified at about 780, 520 and 365 cm^{-1}, respectively. The correlation field splittings of the CO_2 bending vibrations are found to be about 15 cm^{-1}.

Table 3. *Correlation diagram for* $C_2O_4^{-2}$



Modes	Molecular group D_{2h}	Site group C_i	Factor group C_{2h}^5	Activity
ν_1,ν_2,ν_3	A_g	A_g	A_g	Raman
ν_5,ν_6,R_z	B_{1g}			
R_y	B_{2g}		B_g	Raman
ν_7,R_x	B_{3g}			
ν_4	A_u	A_u	A_u	Infrared
ν_8,T_z	B_{1u}			
ν_9,ν_{10},T_y	B_{2u}		B_u	Infrared
ν_{11},ν_{12},T_x	B_{3u}			

The cartesian coordinate system is chosen so that the z-axis is perpendicular to the molecular plane and the y-axis along the C-C direction.

The C—C torsional mode (ν_4) is known to be inactive in both the *Raman* and infrared spectra when the structure of the oxalate ion is D_{2h}. However, this torsional vibration may become optically active with the symmetry lowering of the oxalate ion in the crystal force field.

In deed, the wavenumbers for ν_4 are found to be 148 cm^{-1} for $Na_2C_2O_4$[15], 164 cm^{-1} for $Na_2C_2O_4 \cdot H_2O_2$[15], 232 cm^{-1} for $K_2C_2O_4 \cdot H_2O$[16] and 200 cm^{-1} for $(NH_4)_2C_2O_4 \cdot H_2O$[19]. Since the correlation field effect is also anticipated for this vibrational mode, the infrared broad band at about 290 cm^{-1} is in preference as ν_4 to the simple band at about 215 cm^{-1}.

External Vibrations

In the $Li_2C_2O_4$ crystal, the lithium ion is surrounded tetrahedrally by four oxygen atoms of the oxalate ions with the Li···O internuclear distances from 2.071 to 1.931 Å[13]. Consequently, the Li^- translational lattice vibrations are expected in the wavenumber region above 300 cm^{-1} [4, 5, 8, 20, 21] with the characteristic isotopic wavenumber shifts given by

$$\nu(^6Li)/(^7Li) = \sqrt{m(^7Li)/m(^6Li)} = 1.080,$$

where $m(^nLi)$ indicates the atomic mass of ^nLi. On the other hand, the translational and rotational lattice vibrations of the oxalate ions are expected in the wavenumber region below 300 cm^{-1} [15–19].

As seen in Table 1, there are 12 *Raman* active external vibrations, in which six are the Li^+ translational lattice vibrations and six the $C_2O_4^{-2}$ rotational lattice vibrations. For the Li^+ translational lattice vibrations, the accidental degeneracies are presumed because the lithium ion is placed at the center of the LiO_4 tetrahedron and two lithium ions in the crystal are very far apart. Actually, only one broad band at 468 cm^{-1} of $^6Li_2C_2O_4$ gives the remarkable wavenumber shift upon ^7Li-substitution and the ratio of 468/437 = 1.071 is reasonable to assign this band as the Li^+ translational lattice vibrations. In the *Raman* spectrum below 300 cm^{-1}, there are two weak, two strong and two very strong bands and the bands at 230, 196, 159, 136, 97 and 85 cm^{-1} are assigned with no doubt to the $C_2O_4^{-2}$ rotational lattice vibrations.

As the infrared active external vibrations, there are 9 translational lattice modes. Taking the normal coordinates of the acoustic modes into account, it can be concluded that six external vibrations of nine are adequately approximated by the Li^+ translational lattice vibrations which give the $^6Li/^7Li$ isotopic wavenumber shifts and three external ones by the $C_2O_4^{-2}$ translational lattice vibrations. In analogy with the *Raman* active external vibrations, the broad bands at 460 cm^{-1} of $^6Li_2C_2O_4$ and 435 cm^{-1} of $^7Li_2C_2O_4$ are easily assigned to the Li^+ translational lattice vibrations and the accidental degeneracies are also taken into account. The $^6Li/^7Li$ wavenumber ratio is found to be 460/435 = 1.057 and this value, which is somewhat smaller than that calculated for the *Raman* bands, can be corrected by adding the acoustic modes to complete the normal coordinate system. Finally, three infrared intense bands at 214, 116 and 88 cm^{-1} are attributable as the $C_2O_4^{-2}$ translational lattice vibrations.

In this manner, the effectiveness of use of the $^6Li/^7Li$ isotope effect to analyse the vibrational spectral data was demonstrated for $Li_2C_2O_4$ and the fundamental wavenumbers for the internal and external vibrations were completely found out except for the structures of the Li^+ translational ones.

Acknowledgements

The authors would like to thank Prof. Dr. *K. Kawai* and Dr. *I. Kanesaka* of the Toyama University for the valuable discussions and also Dr. *O. Sala* of the Universidade de São Paulo for permission to use the *Raman* spectrometer. One of us (*Y. H.*) acknowledges the award by the Conselho Nacional do Desenvolvimento Científico e Tecnológico of a research fellowship.

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