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Low Wavenumber *Raman* Bands (300-50 cm^{-1}) for Four Isotopically Substituted Lithium Hydrogen Oxalate Monohydrates $LiXC_2O_4 \cdot X_2O$

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The solid state *Raman* spectra (300-50 cm^{-1}) of lithium hydrogen oxalate monohydrate have been investigated for four isotopically substituted compounds, $^6LiHC_2O_4 \cdot H_2O$, $^7LiHC_2O_4 \cdot H_2O$, $^6LiDC_2O_4 \cdot D_2O$ and $^7LiDC_2O_4 \cdot D_2O$. The observed spectral data have been discussed on the basis of the factor group analysis by considering the H/D and $^6Li/^7Li$ isotope effects on the fundamental lattice vibrations.

(Keywords: H/D *Isotope effect;* $^6Li/^7Li$ *Isotope effect; Lithium hydrogen oxalate monohydrate; Raman spectral data)*

Raman-Banden (300—50 cm^{-1}) von vier isotopensubstituierten Lithiumwasserstoffoxalat-monohydraten $LiXC_2O_4 \cdot X_2O$

Es wurden vier isotopensubstituierte Verbindungen ($^6LiHC_2O_4 \cdot H_2O$, $^7LiHC_2O_4 \cdot H_2O$, $^6LiDC_2O_4 \cdot D_2O$ und $^7LiDC_2O_4 \cdot D_2O$) mittels *Raman*-Festkörper-Spektroskopie im Bereich von 300—50 cm^{-1} untersucht. Die ermittelten Daten werden auf Basis der Faktorengruppenanalyse unter Beachtung der H/D- und $^6Li/^7Li$-Isotopeneffekte diskutiert.

Introduction

Recently, it has been shown for some inorganic lithium compounds that the $^6Li/^7Li$ isotope substitution is very useful in vibrational spectroscopy based on the factor group treatments to analyze the observed spectral data[1–9]. The application of $^6Li/^7Li$ isotope effect combined with the H/D isotope effect was particularly interesting to study the vibrational mode coupling among lattice vibrations since the

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$^6Li/^7Li$ wavenumber shifts were found not only on the Li^+ translation bands but also on the other lattice bands. The *Raman* and infrared spectra of lithium hydrogen oxalate monohydrate were previously reported by *de Villepin* and *Novak*[10] and the observed data were studied by considering the isotope band shifts among $^6LiHC_2O_4 \cdot H_2O$, $^7LiHC_2O_4 \cdot H_2O$ and $^7LiDC_2O_4 \cdot D_2O$. However, the *Raman* spectral data in the low wavenumber region from 300 to 50 cm^{-1} are somewhat different in their band positions and relative intensities from the data measured in our laboratory. These slight differences provide, sometimes, an important change in band assignments.

In the present paper, therefore, the *Raman* spectra in the wavenumber region below 300 cm^{-1} are investigated for four isotopically substituted lithium hydrogen oxalate monohydrates, $^6LiHC_2O_4 \cdot H_2O$, $^7LiHC_2O_4 \cdot H_2O$, $^6LiDC_2O_4 \cdot D_2O$ and $^7LiDC_2O_4 \cdot D_2O$. The observed *Raman* bands are discussed on the experimental and theoretical isotope wavenumber shifts of the fundamental vibrations by considering the results of the factor group analysis.

Experimental

As the starting materials, $^6Li_2CO_3$ was first converted from metallic ^6Li ($> 95.5\%$ enriched) and lithium carbonate commercially obtained with natural abundance was used as $^7Li_2CO_3$. Oxalic acid was twice recrystallized prior to use. $^6LiHC_2O_4 \cdot H_2O$ and $^7LiHC_2O_4 \cdot H_2O$ were prepared by dissolving oxalic acid in hot water and adding an equivalent amount of lithium carbonate. These H_2O-salts were recrystallized from aqueous solution before use. Similarly, the D_2O-salts, $^6LiDC_2O_4 \cdot D_2O$ and $^7LiDC_2O_4 \cdot D_2O$, were obtained by repeated recrystallizations of the H_2O-salts from heavy water ($> 99.8\%$ enriched). The degrees of deuteration were checked by the characteristic infrared bands of the water molecules of crystallization.

The *Raman* spectra of the four isotopically substituted polycrystalline lithium hydrogen oxalate monohydrates were recorded in the 300-50 cm^{-1} region using a Cary 82 laser *Raman* spectrometer equipped with a Spectra Physics 165 argon ion laser (514.5 nm) as the excitation source. To check the relative intensities of the fundamental bands, a Jarrell-Ash 25-300 laser *Raman* spectrometer was also used. The spectral resolution was about 2.0 cm^{-1} for intense bands and about 4.5 cm^{-1} for weak bands.

Results and Discussion

According to the single-crystal X-ray diffraction structural study[11,12], lithium hydrogen oxalate monohydrate crystallizes at room temperature into a triclinic lattice of space group $P1 \equiv C_1^1$ from aqueous solution and the crystallographic unit cell, which is also a primitive unit cell, contains only one formula unit of $LiXC_2O_4 \cdot X_2O$, where X is H or D. The planar hydrogen oxalate ions form layer-like infinite zig-zag chains through short and asymmetric O—H ··· O hydrogen bonds in the [101] direction. The chains are transversely linked by O ··· H—O—H ··· O hydrogen bonds and $O \cdots Li^+ \cdots O$ electrostatic forces. The lithium ion is surrounded in distorted trigonal bipyramidal coordination by five oxygen atoms, the mean distance being about 209 pm. The water molecule of crystallization is in tetrahedral environment of two O ··· H—O—H hydrogen bonds which link the hydrogen oxalate ion chains and two $Li^+ \cdots OH_2$ interactions. In this work, the same crystal structure is assumed for the four isotopically substituted compounds in spite of the slight structural distortion created by isotope substitution.

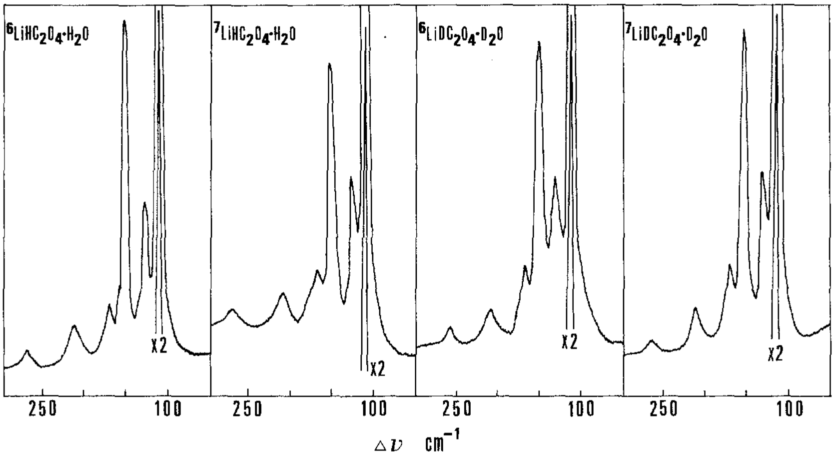

Fig. 1. *Raman* spectra (from 300 to 50 cm^{-1}) of $^6LiHC_2O_4 \cdot H_2O$, $^7LiHC_2O_4 \cdot H_2O$, $^6LiDC_2O_4 \cdot D_2O$ and $^7LiDC_2O_4 \cdot D_2O$

Fig. 1 gives the *Raman* spectra from 300 to 50 cm^{-1} of four isotopically substituted polycrystalline lithium hydrogen oxalate monohydrates, $^6LiHC_2O_4 \cdot H_2O$, $^7LiHC_2O_4 \cdot H_2O$, $^6LiDC_2O_4 \cdot D_2O$ and $^7LiDC_2O_4 \cdot D_2O$. The wavenumbers and relative intensities are summarized in Table 1 together with the band assignments which will be discussed later. Table 2 gives the isotope wavenumber ratios of the fundamental bands.

As seen in Fig. 1 and Table 1, the solid state monohydrate has six *Raman* bands in the wavenumber region below 300 cm^{-1}. The weak bands at about 270, 210 and 170 cm^{-1} clearly show the H/D and $^6Li/^7Li$ isotope band shifts. The bands at about 155 and 130 cm^{-1} are H/D-sensitive only

Table 1. *Observed Raman wavenumbers (in cm^{-1}) for* Li$XC_2O_4 \cdot X_2O$

	$^6LiHC_2O_4 \cdot H_2O$		$^7LiHC_2O_4 \cdot H_2O$		$^6LiDC_2O_4 \cdot D_2O$		$^7LiDC_2O_4 \cdot D_2O$		
ν_1	275	vw	273	vw	261	vw	259	vw	T'
ν_2	216	w	213	w	213	w	210	w	T'
ν_3	174	w	172	w	170	w	168	w	T'
ν_4	154	s	154	s	153	s	153	s	R'
ν_5	130	m	130	m	129	m	129	m	R'
ν_6	115	vs	115	vs	115	vs	115	vs	R'

vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

while the band at 115 cm^{-1}, which is characteristically intense in the *Raman* spectrum, is not affected by any isotope substitution. Our *Raman* spectral data are not so much different from the data by *de Villepin* and *Novak*[10] except that the *Raman* band separations of about 10 cm^{-1} were not observed on the 210 and 170 cm^{-1} bands. The 270 cm^{-1} band seems to have a shoulder band at the high wavenumber side.

Since the *Bravais* unit cell of lithium hydrogen oxalate monohydrate has no symmetry element in the structure and all the sites, Li$^+$, $XC_2O_4^-$ and X_2O, are situated in general site positions, the 30 normal vibrations become active in both the *Raman* and infrared spectra. In the wavenumber region from 300 to 50 cm^{-1}, we can expect only the torsional and wagging modes of internal vibration of the $XC_2O_4^-$ site, the $XC_2O_4^-$ and X_2O site translations and the $XC_2O_4^-$ site rotations[10,13–15].

In consideration of the crystal force field that the hydrogen oxalate ions are strongly linked each other by hydrogen bonds and the lithium sites are substantially ionic in its force environment, it is easily presumed that the $XC_2O_4^-$ internal vibrations are hardly coupled mechanically with the Li$^+$ translational lattice modes and the fundamental bands are expected to be almost ^{6}Li/^{7}Li-insensitive. For the torsional mode, the fundamental band is expected to be also almost H/D-insensitive from the crystal structure[12] and the band intensity should be weak in the infrared and *Raman* spectra because this vibrational mode is both inactive for the free oxalate ion of D_{2h} point symmetry. On the other hand, the wagging modes may be effectively sensitive upon H/D substitution. Hence, the six *Raman* bands in Table 1 can not be considered as the $XC_2O_4^-$ internal ones. The torsional and wagging modes of the $XC_2O_4^-$ site may be found in the region below 300 cm^{-1} as shoulder or very weak *Raman* bands.

Table 2. *Wavenumber ratios for* $LiXC_2O_4 \cdot X_2O$

	$\frac{^6LiHC_2O_4 \cdot H_2O}{^7LiHC_2O_4 \cdot H_2O}$	$\frac{^6LiDC_2O_4 \cdot D_2O}{^7LiDC_2O_4 \cdot D_2O}$	$\frac{^6LiHC_2O_4 \cdot H_2O}{^6LiDC_2O_4 \cdot D_2O}$	$\frac{^7LiHC_2O_4 \cdot H_2O}{^7LiDC_2O_4 \cdot D_2O}$
ν_1	1.007	1.008	1.054	1.054
ν_2	1.014	1.014	1.014	1.014
ν_3	1.012	1.012	1.024	1.024
ν_4	1.000	1.000	1.007	1.007
ν_5	1.000	1.000	1.008	1.008
ν_6	1.000	1.000	1.000	1.000

There are nine site translational degrees of freedom, in which three are acoustic modes and six are optical active modes. As the normal coordinates for acoustic modes are directly given by a simple mass weighted linear combination of Li^+, $XC_2O_4^-$ and X_2O translations along the respective x-, y- and z-axis, the optical active modes are inevitably also given by combining these three site translations. As a consequence of basic cartesian coordinate mixing to make the normal coordinates, we can expect both the H/D and $^6Li/^7Li$ isotope effects on the translational lattice fundamentals. On the basis of the fact that the weight of an $XC_2O_4^-$ site is remarkably larger than that of a Li^+ or X_2O site, however, the six optical vibrations are approximately described as three Li^+ and three X_2O site translations. The translational lattice modes are generally found to be weak in the *Raman* spectrum and intense in the infrared spectrum. The three *Raman* bands at about 270, 210 and 170 cm^{-1} have their infrared counterparts at about 280, 215 and 175 cm^{-1} with relatively strong intensities[10] and are attributable as the translational lattice fundamentals. The isotope band shifts in Table 2 show that the 270 cm^{-1} band is almost the pure X_2O translation because the wavenumber ratios are comparable with the theoretical one of $\sqrt{m(D_2O)/m(H_2O)} = 1.054$, where $m(X_2O)$ is the molecular weight of X_2O site. The 210 and 170 cm^{-1} bands are the well-mixed vibrations of Li^+ and X_2O translations.

The rotational lattice modes are generally intense in the *Raman* spectrum and weak in the infrared spectrum. Based on the crystal force field mentioned earlier to the internal vibrations, the rotational lattice modes of the $XC_2O_4^-$ site are also not effectively influenced in their band positions by $^6Li/^7Li$ substitution. On the other hand, the H/D isotope wavenumber ratios are calculated from inertia momenta of the $XC_2O_4^-$

site to be ca. 1 000 to the axis of the zig-zag chain and ca. 1 006 to the axes perpendicular to the chain. So that, the *Raman* bands at about 155, 130 and 115 cm^{-1}, whose infrared counterparts are at about 155, 135 and 120 cm^{-1} by *de Villepin* and *Novak*[10], are undoubtedly assigned as the $XC_2O_4^-$ rotational lattice modes. The characteristic band at 115 cm^{-1} which is also intense in the infrared spectrum[10] is the rotation of the $XC_2O_4^-$ site zig-zag chain.

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