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Infrared Spectra (700-200 cm^{-1}) and ^{6}Li/^{7}Li and H_2O/D_2O Isotope Effects for Four Isotopically Substituted Lithium Formate Monohydrates

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The infrared spectra, in the 700-200 cm^{-1} region, have been reported for $^6LiHCO_2 \cdot H_2O$, $^6LiHCO_2 \cdot D_2O$, $^7LiHCO_2 \cdot H_2O$ and $^7LiHCO_2 \cdot D_2O$ and the observed fundamental bands have been discussed taking into account the ^{6}Li/^{7}Li and H_2O/D_2O isotope wavenumber shifts on the fundamental vibrations.

(Keywords: H_2O/D_2O *isotope effect; Infrared spectral data;* ^{6}Li/^{7}Li *isotope effect; Lithium formate monohydrate)*

Infrarotspektren (700—200 cm^{-1}) und ^{6}Li/^{7}Li- *und* H_2O/D_2O-*Isotopeneffekte für vier isotopensubstituierte Lithiumformat-monohydrate*

Die Infrarotspektren in der Region von 700—200 cm^{-1} werden für $^6LiHCO_2 \cdot H_2O$, $^6LiHCO_2 \cdot D_2O$, $^7LiHCO_2 \cdot H_2O$ und $^7LiHCO_2 \cdot D_2O$ angegeben und die beobachteten Grundschwingungen zusammen mit den isotopischen Verschiebungen der Wellenzahlen diskutiert.

Introduction

The vibrational spectral data of solid state lithium formate monohydrate (*LFMH*) were first reported by *Cadene*[1] and *Krishnan* and *Ramanujam*[2] and the band assignments were studied for the internal fundamentals. Later, *Galzerani* et al.[3] applied a laser-*Raman* spectroscopy to the *LFMH* single crystals, but the vibrational analysis was limited to the internal modes and the symmetric O—H$\cdots$O hydrogen bond stretching modes. Recently, the external fundamentals in the 300-25 cm^{-1} region were investigated with the aid of *Raman* spec-

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troscopy by *Hase*[4] and the observed bands were analyzed by considering the ^{6}Li/^{7}Li, HCO_2^-/DCO_2^-, and H_2O/D_2O isotope wavenumber shifts.

Thus, using the *Raman* spectral data mainly, the fundamental vibrations of solid state *LFMH* were already studied for the internal fundamentals in the 4000–700 cm^{-1} region and for the external fundamentals in the 300–25 cm^{-1} region. In the present paper, the fundamental bands in the 700–200 cm^{-1} region are investigated by use of infrared spectroscopy and the isotope wavenumber shifts of the fundamental vibrations are discussed for four isotopically substituted lithium formate monohydrates.

Experimental

The preparative procedures of $^6LiHCO_2 \cdot H_2O$, $^6LiHCO_2 \cdot D_2O$, $^7LiHCO_2 \cdot H_2O$ and $^7LiHCO_2 \cdot D_2O$ followed the usual method given elsewhere[4]. The infrared were measured for polycrystalline compounds in the 700–200 cm^{-1} region, on a Perkin-Elmer IR 180 spectrophotometer, as Nujol and Fluorolube mulls between two CsI or polyethylene plates. The spectral resolution for most measurements was typically 1.0 cm^{-1}, but a resolution of about 3.5 cm^{-1} was also used for some shoulder bands.

Results and Discussion

According to the X-ray and neutron diffraction structural studies[5–7], lithium formate crystallizes, as a monohydrate salt, from aqueous solution into an orthorhombic space group $Pnb\,2_1 \equiv C_{2v}^9$ and the primitive unit cell contains four formula units of $LiHCO_2 \cdot X_2O$, where X is H or D. In spite of the slight structural distortion created by isotope substitution, the same crystal structure may be assumed for four isotopically substituted salts. Since the Li^+, HCO_2^-, and X_2O sites are in general positions, the representation of the 93 normal modes of vibration is found to be

$$\Gamma = 23\,a_1 + 24\,a_2 + 23\,b_1 + 23\,b_2$$

and the 69 fundamental modes of the a_1, b_1 and b_2 species are infrared active.

To facilitate the vibrational band analysis, the fundamental vibrations are classified into six classes. The internal fundamentals are observed in the 4000–700 cm^{-1} region[1–3]. The X_2O rotational lattice modes, R′(X_2O), are expected in the 900–400 cm^{-1} region[8] with the notable isotope effects given by $\nu(H_2O)/\nu(D_2O) = \sqrt{I_i(D_2O)/I_i(H_2O)}$, where $I_i(X_2O)$ indicates the inertia momentum of the X_2O site around the molecular axis i, while the X_2O translational lattice modes, T′(X_2O), are expected below 300 cm^{-1} and the isotope wavenumber ratios are found to be $\nu(H_2O)/\nu(D_2O) = \sqrt{m(D_2O)/m(H_2O)}$, where $m(X_2O)$ is the molecular weight of the X_2O site. Since the Li^+ site in the

Table 1. *Isotope effects in wavenumber ratios expected for the lattice vibrations of lithium formate monohydrate* (LiHCO$_2\cdot X_2$O)

		$\frac{^6\mathrm{LiHCO_2.H_2O}}{^6\mathrm{LiHCO_2.D_2O}}$	$\frac{^7\mathrm{LiHCO_2.H_2O}}{^7\mathrm{LiHCO_2.D_2O}}$	$\frac{^6\mathrm{LiHCO_2.H_2O}}{^7\mathrm{LiHCO_2.H_2O}}$	$\frac{^6\mathrm{LiHCO_2.D_2O}}{^7\mathrm{LiHCO_2.D_2O}}$
R'(X$_2$O)	A	1.341	1.341	1.000	1.000
	B	1.414	1.414	1.000	1.000
	C	1.390	1.390	1.000	1.000
R'(HCO$_2^-$)		1.000	1.000	1.000	1.000
T'(Li$^+$)		1.000	1.000	1.080	1.080
T'(X$_2$O)		1.054	1.054	1.000	1.000
T'(HCO$_2^-$)		1.000	1.000	1.000	1.000

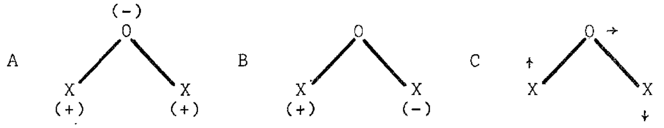

Table 2. *Observed infrared spectral data, in cm^{-1}, and wavenumber ratios for lithium formate monohydrate* (LiHCO$_2\cdot X_2$O)

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
^{6}LiHCO$_2$.H$_2$O	660 s	635 s	495 vs	442 vs	274 s	222 m
^{6}LiHCO$_2$.D$_2$O	580 s,sh	510 s,sh	484 vs	430 vs	265 s	216 m
^{7}LiHCO$_2$.H$_2$O	660 s	635 s	462 vs	420 vs	275 s	222 m
^{7}LiHCO$_2$.D$_2$O	580 s,sh	500 s,sh	460 vs	412 vs	267 s	217 m
iHCO$_2$.H$_2$O/^{6}LiHCO$_2$.D$_2$O	1.138	1.245	1.023	1.028	1.034	1.028
iHCO$_2$.H$_2$O/^{7}LiHCO$_2$.D$_2$O	1.138	1.270	1.004	1.019	1.030	1.023
iHCO$_2$.H$_2$O/^{7}LiHCO$_2$.H$_2$O	1.000	1.000	1.071	1.052	0.996	1.000
iHCO$_2$.D$_2$O/^{7}LiHCO$_2$.D$_2$O	1.000	1.020	1.052	1.044	0.993	0.995
Assignment	R'(X$_2$O)	R'(X$_2$O)	T'(Li$^+$)	T'(Li$^+$)	T'(X$_2$O) + T'(HCO$_2^-$)	T'(X$_2$O) + T'(HCO$_2^-$)

LFMH crystal force field is surrounded almost tetrahedrally by oxygen atoms, the Li^+ translational lattice modes, $T'(Li^+)$, are found in the 600-350 cm^{-1} region[9] and the isotope effects should be $\nu(^6Li)/\nu(^7Li) = \sqrt{m(^7Li)/m(^6Li)}$, where $m(^nLi)$ is the weight of the $^nLi^+$ site. On the other hand, the HCO_2^- rotational and translational lattice modes, $R'(HCO_2^-)$ and $T'(HCO_2^-)$, are found in the region below 300 cm^{-1}[4,10,11] and no isotope band shifts are expected. The wavenumber ratios theoretically calculated for the pure vibrational lattice modes are summarized in Table 1.

The infrared spectral data are listed in Table 2, together with the wavenumber ratios from the experimental band positions. In the present study, from 700 to 200 cm^{-1}, six bands were found for each isotopically substituted salt and the observed bands can be classified into three groups by considering the band positions and the isotope wavenumber shifts. The first group consists of ν_1 and ν_2 and the bands of the H_2O-salts at 660 and 635 cm^{-1} are considerably shifted upon D_2O substitution to 580 and 510/500 cm^{-1}, respectively. Here, it should be noted that the ν_2 band of $^6LiHCO_2 \cdot D_2O$ is 10 cm^{-1} higher than that of $^7LiHCO_2 \cdot D_2O$. Although these bands are undoubtedly assigned to $R'(X_2O)$, a substantial contribution of $R'(HCO_2^-)$ and/or $T'(HCO_2^-)$ must be taken into account to explain the wavenumber ratios from 1.138 to 1.270. Two characteristic bands in the 500-400 cm^{-1} region belong to the second group. The fundamental bands in this wavenumber region are assigned as $R'(X_2O)$ or $T'(Li^+)$. The ν_3 bands are evidently attributable to $T'(Li^+)$ from the wavenumber ratios for $^6LiHCO_2 \cdot H_2O$, $^7LiHCO_2 \cdot H_2O$ and $^7LiHCO_2 \cdot D_2O$. On the other hand, the band position of ν_3 for $^6LiHCO_2 \cdot D_2O$ is found to be 11 cm^{-1} lower than that for $^6LiHCO_2 \cdot H_2O$. This wavenumber lowering can be explained reasonably in terms of the two interacting energy levels between ν_2 and ν_3. From the band positions observed for $^6LiHCO_2 \cdot H_2O$, $^7LiHCO_2 \cdot H_2O$ and $^7LiHCO_2 \cdot D_2O$, the unperturbed wavenumbers for $^6LiHCO_2 \cdot D_2O$ can be presumed to be $\nu_2 = 500$ cm^{-1} and $\nu_3 = 493$ cm^{-1}. Since these vibrational energy levels are considerably close, two fundamental modes can be mixed up when they belong to the same symmetry species. As a result, the perturbed ν_2 and ν_3 bands for $^6LiHCO_2 \cdot D_2O$ are observed at 510 and 484 cm^{-1}, respectively. The ratios $\nu_2'\nu_3'/\nu_2''\nu_3''$ confirm this explanation. The ν_4 bands

$$\nu_2'\nu_3'/\nu_2''\nu_3'' = \begin{array}{l} ^6LiHCO_2 \cdot H_2O/^6LiHCO_2 \cdot D_2O = 1.273 \\ ^7LiHCO_2 \cdot H_2O/^7LiHCO_2 \cdot D_2O = 1.276 \\ ^6LiHCO_2 \cdot H_2O/^7LiHCO_2 \cdot H_2O = 1.071 \\ ^6LiHCO_2 \cdot D_2O/^7LiHCO_2 \cdot D_2O = 1.073 \end{array}$$

are found to be sensitive in their band positions to the H_2O/D_2O substitution as well as to the $^6Li/^7Li$ substitution. From the wavenumber ratios given in Table 2, consequently, the ν_4 bands are assigned as T′ (Li^+) with an important contribution of R′ (X_2O) and/or T′ (X_2O). The third group consists of ν_5 and ν_6 and the infrared bands at about 270 and 220 cm^{-1} are comparable with the *Raman* ones at about 270 and 220/215 cm^{-1} [14]. Because the wavenumber ratios from 1.034 to 1.023 are appreciably smaller by comparison with the theoretical ratios for T′ (X_2O), these fundamental bands are assigned as the vibrational mode mixing bands between T′ (X_2O) and T′ (HCO_2^-).

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