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Raman Spectroscopic Study of Four Isotopically Substituted Lithium Hydroxide Monohydrates

Yoshiyuki Hase

Instituto de Química, Universidade Estadual de Campinas, 13100 Campinas, São Paulo, Brazil

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Raman spectral data of polycrystals of four isotopically substituted lithium hydroxide monohydrates, $^6LiOH \cdot H_2O$, $^7LiOH \cdot H_2O$, $^6LiOD \cdot D_2O$ and $^7LiOD \cdot D_2O$, have been investigated in the 4,000-50 cm^{-1} region. The observed spectra have been analyzed and discussed taking into account the results of the factor group analysis and the H/D and $^6Li/^7Li$ isotope effects on the fundamental wavenumbers.

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

Raman-spektroskopische Untersuchung von vier isotopisch substituierten Lithiumhydroxid-Monohydraten

Raman-spektroskopische Daten von $^6LiOH \cdot H_2O$, $^7LiOH \cdot H_2O$, $^6LiOD \cdot D_2O$ und $^7LiOD \cdot D_2O$ werden im Bereich von 4000 bis 50 cm^{-1} angegeben. Die beobachteten Spektren werden analysiert und im Hinblick auf Faktorgruppenanalyse und auf die Isotopeneffekte H/D und $^6Li/^7Li$ diskutiert.

Introduction

It is well known that lithium hydroxide crystallizes from aqueous solution as a monohydrate salt and that the water molecules of crystallization are easily removed from their lattice points, by heating under reduced pressure, to form an anhydrous salt. In previous investigations, by *Raman* and infrared spectroscopy, of four isotopically substituted anhydrous lithium hydroxides[1, 2], it was found that the wavenumber ratios of some fundamental bands show intricate wavenumber shifts upon H/D or $^6Li/^7Li$ isotope substitution and that these apparently irregular band shifts can be reasonably explained by taking into account the vibrational coupling between the Li^+ trans-

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lational and OH^- (or OD^-) rotational lattice modes. Recently, this fact has been substantiated by normal coordinate calculations[3]. The normal mode analysis for lithium hydroxide monohydrate crystal indicates that the Li^+ translational lattice modes may be coupled mechanically with the H_2O (or D_2O) rotational ones and that complicated isotopic wavenumber shifts are expected for some fundamental bands as a result of the vibrational mode mixing[4]. However, the infrared active fundamental bands of lithium hydroxide monohydrate do not show this type of mode coupling and the observed wavenumber shifts have only shown the characteristic isotope effects[5]. On the other hand, the *Raman* active lattice modes of the monohydrate salt have not as yet been investigated, except for a mercury lamp study by *Krishnamurti*[6].

In this paper, the *Raman* spectra of four isotopically substituted solid state lithium hydroxide monohydrates are reported and the observed bands are assigned by considering the results of the factor group treatments and the H/D and $^6Li/^7Li$ isotopic wavenumber shifts. The vibrational mode coupling between the lattice modes is discussed on the basis of the isotopic wavenumber ratios between two corresponding fundamental bands.

Experimental

$^6LiOH \cdot H_2O$ was prepared by the direct reaction of metallic ^6Li ($> 95.5\%$ enriched) with freshly distilled water. The aqueous solution was evaporated under reduced pressure using a vacuum system until lithium hydroxide monohydrate was crystallized. The crystals obtained were filtered off and dried in a stream of dry nitrogen at room temperature. Lithium hydroxide monohydrate as $^7LiOH \cdot H_2O$ was obtained commercially with natural abundance and recrystallized from aqueous solution before use. The deuterium substituted salts, $^6LiOD \cdot D_2O$ and $^7LiOD \cdot D_2O$, were prepared by repeated recrystallizations of $^6LiOH \cdot H_2O$ and $^7LiOH \cdot H_2O$, respectively, from heavy water ($> 99.8\%$ enriched). The degrees of deuteration were examined by the characteristic infrared band at 3,575 cm^{-1} of $^6LiOH \cdot H_2O$ and $^7LiOH \cdot H_2O$[5, 7] and found to be almost complete.

The *Raman* spectra of polycrystalline lithium hydroxide monohydrates were recorded in the region from 4,000 to 50 cm^{-1} twice, using Jarrell-Ash 25-300 and Cary 82 laser *Raman* spectrometers equipped with an argon ion laser (488.0 and 514.5 nm) as the exciting source. The spectral resolution was typically 2-4 cm^{-1}, but a resolution of about 6 cm^{-1} was also used for weak and broad bands. The observed bands should be accurate to ± 3 cm^{-1}.

Crystal Structure and Normal Mode Analysis

Lithium hydroxide monohydrate crystallizes into a monoclinic lattice of space group $C2/m \equiv C_{2h}^3$ and the crystallographic unit cell contains four formula units of $^7LiOH \cdot H_2O$[8–12]. Fig. 1 shows the arrangement of the atoms in the unit cell determined by the neutron diffraction technique[12]. In the present study, the same crystal structure is assumed for four isotopically substituted crystals in spite of the slight structural distortion created by isotope substitution. The lithium ions are located in a C_2 site and surrounded tetrahedrally by four oxygen atoms. The Li^+—OH_2 and Li^+—OH^- bond lengths of this LiO_4 unit are found to be 198.2 and 196.6 pm, respectively. The site symmetry of the water molecules of crystallization is also known to be C_2 and each molecule forms two equivalent $HO—H\cdots OH^-$ hydrogen bonds. The $O\cdots\cdots O$ distances is about 268 pm. The hydroxide ions are located in the mirror planes and the $O—H^-\cdots OH^-$ hydrogen bonding can be considered to be ineffective because the shortest $O\cdots\cdots O$ distance for this type of interaction is found to be about 319 pm, somewhat longer than twice the van der Waals radius of oxygen[13]. The hydroxide ions in the crystal force field act to link two —Li^+—HOH—Li^+—HOH— infinite zigzag chains.

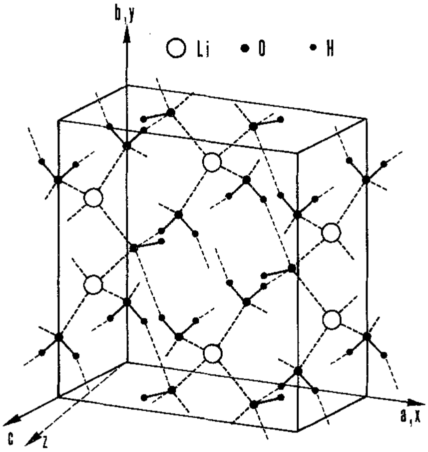

Fig. 1. Crystal structure of lithium hydroxide monohydrate ($LiOX \cdot X_2O$)

Since the crystallographic unit cell of lithium hydroxide monohydrate is base-centered[8–12], a primitive unit cell contains only two formula units and the structure of the reduced representation of the 33 optically active modes of vibration is given by

$$\Gamma = 9\,A_g + 9\,B_g + 6\,A_u + 9\,B_u,$$

in which the vibrational modes of symmetry species A_g and B_g are active in the *Raman* spectrum and those of symmetry species A_u and B_u

are active in the infrared spectrum. Consequently, the 4 internal, 9 translational lattice and 5 rotational lattice modes are expected in the *Raman* spectrum. The acoustic modes belong to symmetry species A_u and B_u. For the vibrational modes of the water molecules of crystallization and the hydroxide ions, the fundamental bands will be shifted upon deuterium substitution, while the characteristic $^6Li/^7Li$ isotope effect is expected in the Li^+ translational lattice modes only.

The results of the factor group analysis are summarized in Table 1, together with the approximate descriptions of the normal modes.

Table 1. *Factor group analysis for lithium hydroxide monohydrate* ($LiOX \cdot X_2O$)

<table>
<tr><th rowspan="2">C_{2h}^3</th><th rowspan="2">N</th><th colspan="2">n</th><th colspan="2">R'</th><th colspan="3">T'</th><th rowspan="2">T</th><th rowspan="2">Activity</th></tr>
<tr><th>OX^-</th><th>X_2O</th><th>OX^-</th><th>X_2O</th><th>Li^+</th><th>OX^-</th><th>X_2O</th></tr>
<tr><td>A_g</td><td>9</td><td>1</td><td>2</td><td>1</td><td>1</td><td>1</td><td>2</td><td>1</td><td>0</td><td>Raman</td></tr>
<tr><td>B_g</td><td>9</td><td>0</td><td>1</td><td>1</td><td>2</td><td>2</td><td>1</td><td>2</td><td>0</td><td>Raman</td></tr>
<tr><td>A_u</td><td>6</td><td>0</td><td>2</td><td>1</td><td>1</td><td colspan="3">2</td><td>1</td><td>Infrared</td></tr>
<tr><td>B_u</td><td>9</td><td>1</td><td>1</td><td>1</td><td>2</td><td colspan="3">4</td><td>2</td><td>Infrared</td></tr>
</table>

N, number of vibrational degrees of freedom; n, number of internal modes; R', number of rotational lattice modes; T', number of translational lattice modes; T, number of acoustic modes.

Results and Discussion

Table 2 gives the wavenumbers and relative intensities of the *Raman* bands from 4,000 to 50 cm^{-1} of four isotopically substituted lithium hydroxide monohydrates, $^6LiOH \cdot H_2O$, $^7LiOH \cdot H_2O$, $^6LiOD \cdot D_2O$ and $^7LiOD \cdot D_2O$, together with the band assignment. Table 3 gives the isotopic wavenumber ratios of the fundamental bands.

The fundamental bands of the four *Raman* active internal modes, three of water molecules and one of hydroxide ions, are found in the wavenumber region above 1,000 cm^{-1} and the characteristic H/D isotope effect is expected in these vibrations. However, as seen in Table 2, only two *Raman* bands were observed in this wavenumber region. A very intense band at 3,566 cm^{-1} of $^6LiOH \cdot H_2O$ and $^7LiOH \cdot H_2O$ shows an isotopic wavenumber shift upon deuterium

Table 2. *Raman spectral data in cm^{-1} for lithium hydroxide monohydrate* (LiO$X \cdot X_2$O)

^{6}LiOH.H$_2$O	^{7}LiOH.H$_2$O	^{6}LiOD.D$_2$O	^{7}LiOD.D$_2$O			
3566 vs	3566 vs	2632 vs	2632 vs	ν_1	A$_g$	νOX$^-$
1090 w	1090 w	1090 w	1090 w		impurity	
842 m	841 m	624 m	624 m	ν_2	A$_g$	R'X$_2$O
703 w,br	696 w,br	468 m	461 m	ν_3^*	B$_g$	R'X$_2$O
597 vw	593 vw	475 w,sh		ν_4^*	B$_g$	R'X$_2$O
542 m	516 m	590 m	565 m	ν_5^*	B$_g$	T'Li$^+$
414 m	394 m	389 m	381 m	ν_6^*	B$_g$	T'Li$^+$
389 m	368 m		368 m	ν_7	A$_g$	T'Li$^+$
248 m	248 m	239 m	239 m	ν_8		T'OX$^-$ and T'X$_2$O
214 m	214 m	206 m	206 m	ν_9		
145 s	145 s	140 s	140 s	ν_{10}		
119 m	119 m	116 m	116 m	ν_{11}		
96 w	96 w	93 w,sh	93 w,sh	ν_{12}		
86 m	86 m	84 m	84 m	ν_{13}		

v, very; s, strong; m, medium; w, weak; sh, shoulder band; br, broad band. (* see text)

substitution. The band observed for ^{6}LiOD · D$_2$O and ^{7}LiOD · D$_2$O is at 2,632 cm^{-1}. According to the relation between the O····O interatomic distances and O—H stretching wavenumbers of the O—H···O hydrogen bond system[14–16], the fundamental bands of the H$_2$O and OH$^-$ stretching vibrations are expected in the 2,900 and 3,600 cm^{-1} regions, respectively, because of their shortest O····O distances of about 268 and 319 pm[12]. Therefore, the *Raman* bands observed at 3,566 and 2,632 cm^{-1} are easily assigned to the OH$^-$ and OD$^-$ stretching modes (A$_g$). It is notable that the fundamental wavenumbers of the *Raman* active OH$^-$ and OD$^-$ stretching modes are very close to those of the infrared active ones[5] at 3,575 and 2,632 cm^{-1}. The isotopic wavenumber ratios calculated from the observed *Raman* bands and obtained theoretically for the normal mode are $\nu(\mathrm{OH}^-)/\nu(\mathrm{OD}^-) = 1.355$ and

Table 3. *Isotopic wavenumber ratios of fundamental bands*

	$^{6}LiOH.H_2O$ / $^{7}LiOH.H_2O$	$^{6}LiOD.D_2O$ / $^{7}LiOD.D_2O$	$^{6}LiOH.H_2O$ / $^{6}LiOD.D_2O$	$^{7}LiOH.H_2O$ / $^{7}LiOD.D_2O$
ν_1	1.000	1.000	1.355	1.355
ν_2	1.001	1.000	1.349	1.348
ν_3	1.010	1.015	1.502	1.510
ν_4	1.007	1.030	1.257	1.286
ν_5	1.050	1.044	0.919	0.913
ν_6	1.051	1.021	1.064	1.034
ν_7	1.057	1.057	1.000	1.000
ν_8	1.000	1.000	1.038	1.038
ν_9	1.000	1.000	1.039	1.039
ν_{10}	1.000	1.000	1.036	1.036
ν_{11}	1.000	1.000	1.026	1.026
ν_{12}	1.000	1.000	1.032	1.032
ν_{13}	1.000	1.000	1.024	1.024
$\nu_3 \times \nu_5$	1.061	1.060	1.380	1.379
$\nu_4 \times \nu_6$	1.058	1.052	1.338	1.330
$\nu_3 \times \nu_6$	1.061	1.037	1.599	1.561
$\nu_4 \times \nu_5$	1.057	1.076	1.155	1.175

$\sqrt{(\mu_O + \mu_H)/(\mu_O + \mu_D)} = 1.374$, respectively. Here, μ is the reciprocal atomic mass. On the other hand, a weak *Raman* band observed at 1,090 cm^{-1} does not undergo a wavenumber shift upon any isotope substitutions and is assigned undoubtedly as an impurity band. The most reasonable assignment for this band is to the totally symmetric CO_3^{-2} stretching vibration of anhydrous lithium carbonate, which often contaminates the lithium hydroxide monohydrate crystal during preparation. In the previous vibrational investigation of anhydrous lithium carbonate[17], the fundamental wavenumbers of this *Raman* intense mode were found at 1,092 cm^{-1} for $^6Li_2CO_3$ and at 1,091 cm^{-1} for $^7Li_2CO_3$. The fundamental bands of the water molecules of crystallization, $\nu_a X_2O$ (B_g), $\nu_s X_2O$ (A_g) and δX_2O (A_g), were not observed in the present study.

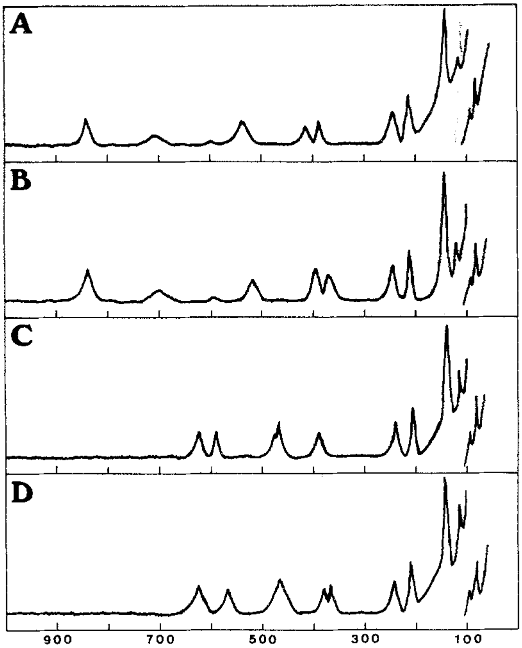

Fig. 2. *Raman* spectra from 1,000 to 50 cm^{-1} of *A* $^6LiOH \cdot H_2O$, *B* $^7LiOH \cdot H_2O$, *C* $^6LiOD \cdot D_2O$, and *D* $^7LiOD \cdot D_2O$

In the wavenumber region below 1,000 cm^{-1}, only the bands due to the lattice vibrations are expected. Fig. 2 gives the *Raman* spectra from 1,000 to 50 cm^{-1} of four isotopically substituted lithium hydroxide monohydrates.

Since the hydroxide site in the lithium hydroxide monohydrate crystal force field is not effectively hydrogen bonded through the hydrogen or deuterium atom and the center of gravity of this site is almost located on the oxygen atom, two *Raman* active OH^- or OD^- rotational lattice modes (A_g and B_g) are assumed to be accidentally degenerated and the fundamental bands are expected in the same wavenumber region with those of the infrared active modes (A_u and B_u). In the infrared spectra[5], the OH^- and OD^- rotational lattice modes were observed at 994 cm^{-1} for $^6LiOH \cdot H_2O$ and $^7LiOH \cdot H_2O$ and at 730 cm^{-1} for ^{6}LiOD·D$_2$O and ^{7}LiOD·D$_2$O. However, no *Raman* bands were found in these wavenumber regions and which may be explained by their considerably weak *Raman* intensities.

The H$_2$O rotational lattice vibrations as wagging (B$_g$, rotation about the x-axis), twisting (A$_g$, rotation about the y-axis) and rocking (B$_g$, rotation about the z-axis) modes are expected in the 900-550 cm^{-1} region and the D$_2$O rotational lattice vibrations in the 650-400 cm^{-1} region[5]. The H/D isotopic wavenumber ratios calculated from the inertia momenta for the pure rotational normal modes are 1.341, 1.414 and 1.389, respectively. On the other hand, three Li$^+$ translational lattice vibrations in LiO$_4$ unit are found in the 550-300 cm^{-1} region[5, 17–22] with the ^{6}Li/^{7}Li isotopic wavenumber ratios of $\sqrt{m_{(^7\mathrm{Li})}/m_{(^6\mathrm{Li})}} = 1.080$, where m is the atomic mass. Consequently, the assignment of these lattice modes for the normal salts can be made without difficulties, but a careful analysis is required on the data of the deuterated salts.

The *Raman* bands of ^{6}LiOH·H$_2$O observed at 842, 703 and 597 cm^{-1} and those of ^{7}LiOH·H$_2$O at 841, 696 and 593 cm^{-1} are unquestionably assigned to the H$_2$O rotational lattice modes, in spite of the slight ^{6}Li/^{7}Li isotopic wavenumber shifts. On the other hand, three medium intensity bands of ^{6}LiOH·H$_2$O at 542, 414 and 389 cm^{-1} are characteristically shifted by ^{7}Li substitution and the corresponding fundamental bands of ^{7}LiOH·H$_2$O are found at 516, 394 and 368 cm^{-1}. The ratios calculated from these observed wavenumbers are 1.050, 1.051 and 1.057, respectively, and the values are reasonable for the Li$^+$ translational lattice modes.

By the direct comparison of the observed spectral data for the deuterated salts with the fundamental wavenumbers for the normal salts, the bands at 624 cm^{-1} of ^{6}LiOD·D$_2$O and ^{7}LiOD·D$_2$O are easily assigned to the D$_2$O rotational lattice mode and the bands at 389 cm^{-1} of ^{6}LiOD·D$_2$O and 368 cm^{-1} of ^{7}LiOD·D$_2$O to the Li$^+$ translational lattice mode. However, the assignment of the *Raman* bands observed at 590, 475 and 468 cm^{-1} for ^{6}LiOD·D$_2$O and at 565, 461 and 381 cm^{-1} for ^{7}LiOD·D$_2$O is complicated by the vibrational mode mixings arised from the mechanical coupling. Taking the wavenumbers and relative intensities into account, it becomes apparent that a medium intensity band at 590 cm^{-1} forms a pair with that at 565 cm^{-1} and a band at 468 cm^{-1} with that at 461 cm^{-1}. On the assumption that the ^{6}Li/^{7}Li wavenumber shift should not be unnaturally large even when it is coupled with the H/D isotope effect, an accidental degeneracy is supposed on the bands at 389 cm^{-1} of ^{6}LiOD·D$_2$O and 461 cm^{-1} of ^{7}LiOD·D$_2$O to relate them with the remained bands at 381 cm^{-1} of ^{7}LiOD·D$_2$O and 475 cm^{-1} of ^{6}LiOD·D$_2$O, respectively.

It is readily understood from the atomic displacements illustrated in Fig. 3 that the mechanical coupling between the H_2O or D_2O rotational and Li^+ translational lattice modes takes place with the vibrations of symmetry species B_g, but less is probable with the vibrations of symmetry species A_g. Therefore, the bands ν_2 and ν_7 in Table 2 are attributable, respectively, as the twisting mode of the water molecules of crystallization and the Li^+ translational lattice mode along the y-axis. While, the bands ν_3, ν_4, ν_5 and ν_6 are assigned to the fundamental vibrations of symmetry species B_g. According to the model calculation of the vibrations of water molecule in a tetrahedral environment by

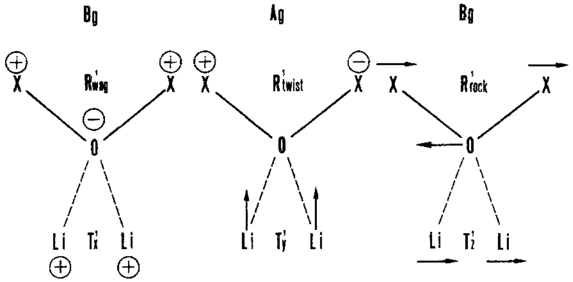

Fig. 3. Vibrational mode mixing between the X_2O rotational and Li^+ translational lattice modes

Eriksson and *Lindgren*[23], the rocking mode has the lowest wavenumber among the three rotational lattice modes. Consequently, the bands ν_3 and ν_4 are assigned rather tentatively as the wagging and rocking modes, respectively. As seen in the last part of Table 3, the combinations of ν_3 with ν_5 and of ν_4 with ν_6 reproduce the H/D and $^6Li/^7Li$ isotope effects better than those of ν_3 with ν_6 and of ν_4 with ν_5. In this study, the bands ν_5 and ν_6 are considered to be the Li^+ translational lattice modes along the x- and z-axis, respectively. The band assignment of symmetry species B_g in Table 2 is substantially true for $^6LiOH \cdot H_2O$ and $^7LiOH \cdot H_2O$, however it is only an approximate description for $^6LiOD \cdot D_2O$ and $^7LiOD \cdot D_2O$ because of the considerable mode mixings between ν_3 and ν_5 and between ν_4 and ν_6. The mechanical coupling becomes stronger in the deuterium substituted salts in comparison with that in the normal ones because of the H/Li and D/Li atomic mass differences.

Three OH^- and OD^- translational and three H_2O and D_2O translational lattice modes are expected in the wavenumber region below 350 cm^{-1}. The theoretical H/D isotopic wavenumber ratios for the pure translational normal modes, calculated from the molecular weight, are $\sqrt{m_{(\mathrm{OD}^-)}/m_{(\mathrm{OH}^-)}} = 1.029$ for the former and $\sqrt{m_{(\mathrm{D_2O})}/m_{(\mathrm{CH_2O})}} = 1.054$ for the latter. Indeed, six *Raman* bands were observed in this wavenumber region for each lithium hydroxide monohydrate salt and the wavenumber ratios for the observed bands vary from 1.039 to 1.024. Probably these translational lattice modes are coupled among them to make the fundamental modes. No evidence was found for the mechanical coupling with the Li^+ translational and the H_2O or D_2O rotational lattice modes.

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