Raman spectra of lithium compounds

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Abstract. The paper is devoted to the results of investigating the spontaneous Raman scattering spectra in the lithium compounds crystals in a wide spectral range by the fibre-optic spectroscopy method. We also present the stimulated Raman scattering spectra in the lithium hydroxide and lithium deuteride crystals obtained with the use of powerful laser source. The symmetry properties of the lithium hydroxide, lithium hydroxide monohydrate and lithium deuteride crystals optical modes were analyzed by means of the irreducible representations of the point symmetry groups. We have established the selection rules in the Raman and infrared absorption spectra of LiOH, LiOH H₂O and LiD crystals.

1. Introduction and background

The studies of the Raman spectra of lithium compounds with hydrogen and hydroxyl groups [1-3] are of great current interest due to the wide use of these crystals in the area of hydrogen energy and in other applications [4, 5]. In addition, the study of the lithium structures crystalline lattices dynamics is important thanks to the high mobility of lithium and the respective crystal lattices instability [6]. To date, the Raman spectrum of these crystals has not been well studied [7-9] and needs further clarification.

In this paper we present the results of the experimental studies of the spontaneous Raman scattering spectra of lithium hydroxide (LiOH), lithium hydroxide monohydrate (LiOH H₂O) and lithium deuteride (LiD) as well as the stimulated Raman scattering spectra of lithium hydroxide (LiOH) and lithium deuteride (LiOD).

2. Experimental technique
The schematic diagram of the experimental setup for the excitation and detection of the spontaneous Raman scattering spectra is shown in Figure 1a. The excitation and registration of the Raman spectra was carried out with the use of the fiber-optical recording technique [10]. As a source of excitation radiation we used the laser with the wavelength $\lambda=785\text{nm}$ and the power of 200 mW. The laser (1) light was directed into the optical fiber (2) and the probe (3) (see Figure 1a). The radiation was focused by the lens (5) on the sample (6) which has the form of polycrystalline powder. The Raman signal arising in the sample was sent to the second optical fiber (8) and filtered in the focusator (9) by means of the photonic crystal (11) and then it entered the input of the minispectrometer (13) with the multielement receiver. The computer (14) has been designed for digital processing and storage of Raman spectra. The exposure time was 1-10 s. The Raman signal was recorded by a small amount (less than 1mg) of the polycrystalline sample.

The stimulated Raman scattering spectra of lithium hydroxide and lithium deuteride were studied using the experimental setup [11], the schematic of which is given in Figure 1b. The stimulated Raman scattering spectra were excited by the giant pulses of the second optical harmonic (532 nm) of a Nd$^{3+}$:YAG laser (1). Through the semitransparent mirror (2) the laser beam was focused by the lens (3) onto the sample (5) and then was brought to the minispectrometer (8). The stimulated Raman scattering in the “backward” geometry was brought to the entrance slit of the minispectrometer (10) after reflecting at the mirror (2).

3. Experimental results and discussion

The spontaneous Raman scattering spectra of lithium hydroxide, lithium hydroxide monohydrate and lithium deuteride obtained at room temperature are shown in Figure 2a-c.
Figure 2. The spontaneous Raman scattering spectra of lithium compounds containing the hydroxyl groups, recorded at room temperature: a) lithium hydroxide; b) lithium hydroxide monohydrate; c) lithium deuteride. The data about the dispersion branches from the work [12] were presented at the inset in the upper right corner of Figure 2c.
As we can see from Figure 2, in the low-frequency Raman spectra of these crystals there are a large number of lines, the most intense of which has a frequency of 328 cm\(^{-1}\).

The spectra of the stimulated Raman scattering in lithium hydroxide and lithium deuteride were shown in Figure 3a, b.

![Figure 3](image-url)

**Figure 3.** The stimulated Raman scattering spectra in lithium compounds: a) lithium hydroxide; b) lithium deuteride.
As we can see from Figure 3b, the first and the second order of the Stokes lines are manifested in the stimulated Raman scattering spectra of lithium hydroxide and lithium deuteride.

The types of the lithium compound primitive cells are presented in Figure 4.

![Figure 4](image_url)

**Figure 4.** The types of the lithium compound primitive cells: a) lithium hydroxide; b) lithium hydroxide monohydrate; c) lithium deuteride.

LiOH crystals have a tetragonal structure (see Figure 4a) which is characterized by the space group symmetry $D_{4h}^7$ ($P_{4_{2}2_{1}}2_{1}$) and contains two formula units. The OH$^-$ ions are located in positions with the symmetry $C_{4v}$ [1].

We have analyzed the symmetry properties of the LiOH optical modes, classified these modes with the aid of the irreducible representations of the group $D_{4h}^7$ and set the selection rules in the Raman and infrared absorption spectra. The results of the group-theoretic analysis are presented in Table 1.

| The space group symmetry of the crystal LiOH – $D_{4h}^7$ | E | $C_{4v}^{1}$ (z) | $C_{2}$ | $2C_{2}'$ | $\sigma_{h}$ | $2\sigma_{v}$ | $2\sigma_{d}$ | $S_{4}^{2}$ | I |
|---|---|---|---|---|---|---|---|---|---|
| $\alpha$ | 0:0:0 | 0:0:0 | 0:0:0 | 0:0:0 | 0:0:0 | 0:0:0 | 0:0:0 | 0:0:0 | 0:0:0 |
| $n_0$ | 6 | 4 | 6 | 0 | 0 | 0 | 6 | 4 | 2 | 0 |
| $n_0 - 1$ | 5 | 3 | 5 | -1 | -1 | -1 | 5 | 3 | 1 | -1 |
| $\chi_{V}$ | 3 | 1 | -1 | -1 | 1 | 1 | 1 | -1 | -3 |
| $\chi_{opt}$ | 15 | 3 | -5 | 1 | -1 | -1 | 5 | 3 | -1 | 3 |

$^a$ $\alpha$ – translation vector.

$^b$ $n_0$ – the number of atoms remaining in place under the transformations of the symmetry.

$^c$ $\chi_{V}$ – the character of the vector representation.

$^d$ $\chi_{opt}$ – the character of the optical representation.
As a result of the analysis it is established that the vibrational representation contains the following types of optical modes:

\[ T_{\text{opt}} = 2A_{1g} (\text{Raman}) + B_{1g} (\text{Raman}) + 2A_{2u} (\text{Infrared}) + 3E_{g} (\text{Raman}) + 2E_{u} (\text{Infrared}) \]  

(1)

Lithium hydroxide monohydrate crystallizes in the monoclinic space group $C_{2h}$ with two formula units in the primitive cell at room temperature (see Figure 4b) [13]. The lithium ions and water molecules have a symmetry $C_2(Z)$, and the hydroxyl ions are lying in a mirror plane [14].

The results of the group-theoretical analysis of optical modes in lithium hydroxide monohydrate are presented in Table 2.

**Table 2.** The results of group-theoretical analysis of optical modes in lithium hydroxide monohydrate.

| Space group symmetry of the crystal LiOH·H₂O–C\(^{3}_2\) | E \(0;0;0\) | C\(_2\)(z) \(0;0;0\) | $\sigma_h$ \(0;0;0\) | I \(0;0;0\) |
|---|---|---|---|---|
| $\tilde{a}$ | 12 | 4 | 4 | 0 |
| $n_0$ | 11 | 3 | 3 | −1 |
| $n_0$\(|-1\) | 3 | −1 | 1 | −3 |
| $\varepsilon_{v}$ | 3 | 1 | 3 | 6 |
| $\varepsilon_{vb}$ | 6 | 2 | 2 | 6 |
| $\varepsilon_{opt}$ | 33 | −3 | 3 | 3 |
| $\varepsilon_{tr}$ | 15 | −3 | 1 | 3 |
| $\varepsilon_{lib}$ | 10 | −2 | 0 | 0 |

\(a\) $\varepsilon_{v}$ – the character of pseudovector representation.

\(b\) $\varepsilon_{[\nu]}$ – the character of the second rank symmetrical tensor.

\(c\) $\varepsilon_{tr}$ – the character of translational representation.

\(d\) $\varepsilon_{lib}$ – the character of the librational representation.

The following types of vibrations are present in the spectrum of lithium hydroxide monohydrate optical vibrations:

\[ T_{\text{opt}} = 9A_{1g} (\text{Raman}) + 9B_{1g} (\text{Raman}) + 6A_{2u} (\text{Infrared}) + 9B_{2u} (\text{Infrared}) \]  

(2)

The structure of irreducible representations corresponding to the librational $T_{\text{lib}}$, translational $T_{\text{tr}}$, internal $T_{\text{int}} = T_{\text{lib}} + T_{\text{tr}}$, and external $T_{\text{ext}} = T_{\text{opt}} - T_{\text{int}}$ types of lithium hydroxide monohydrate vibrations is shown in Table 3.
The lattice modes corresponding to the lithium ions of the hydroxyl group OH\(^-\) and water molecules translations as well as to the water molecules and hydroxyl groups librations are detected in the spontaneous Raman scattering spectra of LiOH·H\(_2\)O.

The lithium deuteride crystals have a sodium chloride type structure (see Figure 4c) characterized by the space group symmetry \(O_h^1\) [15]. In the elementary cubic cell there is one formula unit, and the phonon dispersion curve has three optical branches:

\[
T_{\text{opt}} = F_{1u} (\text{Infrared}) \tag{3}
\]

According to the selection rule, for a perfect crystal of lithium deuteride the optical modes are forbidden in the Raman spectrum of LiD at \(\Gamma\)-point. However, as can be seen from the experimental spectrum (see Figure 2c), there are several Raman peaks with spectral positions close to the phonon frequencies at Brillouin zone edge (see upper inset in Figure 2c). Such effect may be explained as the result of the lattice disturbance due to disordering of lithium and deuterium ions.

4. Conclusions
We have detected the sharp lines of Raman scattering for all discussed crystals. The results allow characterizing the samples of lithium compounds with hydrogen and hydroxyl groups. It is necessary for their effective use. We have presented the results of the stimulated Raman scattering of lithium hydroxide and lithium deuteride. The isotopes influence on the Raman spectrum in the peak positions has been established.

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