Combination bands of libration + vibration of OH/OD centres in ABO₃ crystals

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Abstract. The presence of hydrogen (deuterium) defects in oxide ABO₃ crystals is revealed by a characteristic OH (OD) stretching vibration near 3500 cm^{-1} (2600 cm^{-1}). Low-frequency OH (OD) librational modes have not been reported so far for these crystals. However, we have found in a number of ABO₃ crystals (LiNbO₃, LiTaO₃, SrTiO₃ and KTaO₃) weak high-energy sidebands to the stretching vibration with positions shifted by about 950 cm^{-1} for OH and about 700 cm^{-1} for OD from the vibrational band position. The bandshape of these new OH/OD absorption bands is similar to the bandshape of the OH/OD absorption bands of the stretching vibration in the corresponding ABO₃ crystals. The polarization of these sidebands in general is different from the stretching vibration and reflects more the properties of a three-dimensional oscillator. While the OH/OD stretching vibrations in LiNbO₃ and LiTaO₃ are completely polarized perpendicular to the ferroelectric z-axis, the libration + vibration combination bands exhibit in both crystal systems an intensity ratio $I_{\parallel}/I_{\perp} \sim 0.55$ for OH and an intensity ratio $I_{\parallel}/I_{\perp} \sim 0.75$ for OD with respect to the ferroelectric z-axis. These different intensity ratios for OH and OD support the identification of the new absorption bands as libration + vibration combination bands of the OH (OD) oscillator. The OH/OD libration + vibration combination bands have also been detected as sidebands to higher vibrational transitions in proton- (deuteron-) exchanged LiNbO₃. In a first approximation the energetic positions of the observed OH and OD combination bands can be well described with a simple oscillator model for the libration. The intensity of these sidebands is directly proportional to the intensity of the stretching vibration (or the concentration) of the H (or D) centres.

1. Introduction

Hydrogen, being present in nearly all ABO₃ compounds, forms an OH impurity complex and influences physical properties and applications. For example in LiNbO₃ it influences the laser optical damage [1, 2], the thermal fixing [3] of volume phase holograms (in LiNbO₃:Fe) [4], the dark conductivity [5], the production of waveguiding layers by proton implantation [6], proton exchange [7], the quality of Ti-indiffused optical waveguides [8, 9] and the phase-matching temperature for optical second-harmonic generation [10, 11].

Hydrogen centres in the ABO₃ crystals exhibit a characteristic OH stretching vibration at about 3500 cm^{-1}. In the ferroelectric materials LiNbO₃ and LiTaO₃ the OH absorption band is completely polarized perpendicular to the polar z-axis [12].

High OH (OD) concentrations in surface layers in congruent LiNbO₃ can be prepared by proton/deuteron exchange [7]. The associated broad OH (OD) stretching vibrations (FWHM ≈ 30 (21) cm^{-1}) are again polarized perpendicular to the z-axis, and the absorption maximum shifts to 3508 (2589) cm^{-1} [11, 13, 14].

The librational motion is an important parameter for the model discussion [15] of the OH (OD) defects and their protonic mobility in ABO₃ crystals [5]. The identification of

the libration + vibration combination band in $LiNbO_3$, $LiTaO_3$, $SrTiO_3$ and $KTaO_3$ will be the topic of this paper. To identify the OH (OD) librational motion we investigate the concentration dependence, the polarization dependence and the influence of a tempering process of the libration + vibration combination band reported here for the first time for the perovskite-type crystals mentioned above.

2. Experimental techniques

For the investigations of the OH/OD absorption bands in the bulk of stoichiometric $LiNbO_3$ we use congruent $LiNbO_3$ (48.6 mol% Li_2O) which has been treated by the vapour-transport equilibration (VTE) technique [16, 17, 18] in our own laboratory. The crystals are heated in a lithium-rich atmosphere at 1100 °C, surrounded by a lithium-rich $LiNbO_3$/Li_3NbO_4 powder with Li_2CO_3 and Nb_2O_5 as starting materials. Measurements of spatially resolved second-harmonic generation (SHG) intensity for the $LiNbO_3$ crystals treated using the VTE technique exhibit a phase-matching temperature $T_{PM} \approx 240$ °C for 1064 nm radiation of a Nd:YAG laser, pointing to a nearly stoichiometric and rather homogeneous composition [17, 18].

To get proton- (deuteron-) exchanged $LiNbO_3$:PE (DE) with high optical densities for the OH (OD) stretching vibration we put thin z-cut samples for 70 h in pure benzoic (D-benzoic) acid melt at 517 K. The exchanged layers ($Li^+ \leftrightarrow H^+$) have a thickness of about $d \approx 10$ μm with an absorption coefficient of $\alpha_{max,OH} \approx 9 \times 10^3$ cm^{-1} ($\alpha_{max,OD} \approx 7 \times 10^3$ cm^{-1}) [11]. For our subsequent tempering investigations we fabricate proton-exchanged surface layers with a thickness $d \approx 1.5$ μm (exchange process time: ~4 h).

To raise the hydrogen or deuterium concentration in the bulk of nearly stoichiometric (VTE) $LiNbO_3$ the method of field-supported proton diffusion was employed [1, 12]. An electric DC field (400 V cm^{-1}) was applied perpendicular to the ferroelectric z-axis at $T = 650$ °C for about 20 min in humid atmosphere. This treatment yielded absorption coefficients of the OH stretching vibration up to $\alpha_{max,OH} \approx 15$ cm^{-1} in the bulk of the crystals.

The infrared absorption spectra were obtained with a Fourier–IR spectrometer (113 Cv Bruker) in the range from 2400 cm^{-1} to 7900 cm^{-1} with a resolution up to 0.05 cm^{-1}. For the investigations of the polarization dependence of the absorption bands a wire grid polarizer (Perkin–Elmer) was employed.

3. Results and discussion

3.1. A simple librational oscillator model

A librational motion for OH centres in TiO_2 has been suggested by Bates *et al* [15] to explain the small, anisotropic attempt frequency in a model of thermally activated hopping motion for the protonic mobility. This model resolves the discrepancy between the large depth V_e of the potential of the anharmonic vibrational OH oscillation and much smaller values of the activation energy E_A for the protonic mobility at elevated temperatures. Similar properties are also observed for OH and OD centres in $LiNbO_3$ with $E_A \approx 1.2$ eV and $V_e \approx 4.5$ eV [5, 12]. We therefore want to apply the above random-walk model which yields for thermally activated diffusion in one direction

$$D = D_0 \exp\left(-\frac{E_A}{k_B T}\right) \qquad \text{with } D_0 = \frac{1}{2} v_a d^2 \qquad (1)$$

for the pre-exponential factor D_0 of the Arrhenius expression of the diffusion constant D. Here d signifies the jump distance and ν_a the attempt frequency, i.e. the number of attempts made to surmount the energy barrier [15].

For the protonic properties in TiO₂ Bates *et al* [15] calculated two different librational frequencies parallel $\omega_\parallel$ and perpendicular $\omega_\perp$ to the z-axis for the torsional OH motion, leading consequently to an anisotropic activation energy $(E_A^\parallel \neq E_A^\perp)$ in agreement with experiment. However, the librational absorption could not then be verified experimentally in TiO₂. In LiNbO₃ the activation energy $E_A \approx 1.2$ eV for OH and OD was found to be equal for both isotopes and, moreover, isotropic $(E_A^\parallel = E_A^\perp)$. This property supports the conclusion that the OH stretching vibration, being polarized completely perpendicular to the z-axis, cannot be the attempt frequency as suggested for OH in KTaO₃ [19]. Rather it must be concluded that an isotropic librational motion $(\omega_\parallel = \omega_\perp)$ should exist for OH and OD in LiNbO₃. The observation of the weak direct librational transition in the FIR region is rather difficult and therefore we looked for and report here the results for the combination band of the stretching vibration with the libration.

In a first approximation the librational wavenumber $\bar{\nu}_{lib}$ can be expressed in terms of a simple harmonic oscillator potential $V(\theta) = \frac{1}{2}C\theta^2$ [20]:

$$\bar{\nu}_{lib} = \frac{\nu_{lib}}{c} = \frac{1}{c\,2\pi}\sqrt{\frac{C}{J}} \tag{2}$$

with the moment of inertia $J = \mu_m r_e^2$, where μ_m = reduced mass and r_e = O–H equilibrium distance. Quantum mechanically in the *n*-vibrational state $|\psi_n\rangle$ the effective value of $\bar{\nu}_{lib}$ is defined in terms of the expectation value $\langle\psi_n|1/r^2|\psi_n\rangle$. Furthermore, there exists a dependence on the librational wavenumber $\bar{\nu}_{lib,n}$ from the vibrational state n of the oscillator:

$$\bar{\nu}_{lib,n} = \frac{1}{2\pi c}\sqrt{\frac{C}{J}} = \frac{1}{2\pi c}\sqrt{\frac{C}{\mu_m}\langle\psi_n|1/r^2|\psi_n\rangle}. \tag{3}$$

From equation (3), there will be a difference in wavenumber between (i) the direct librational wavenumber $\bar{\nu}_{lib,0}$ and (ii) the difference in wavenumbers $\bar{\nu}_{lib,n} \equiv \bar{\nu}_{vib_{0n}+lib} - \bar{\nu}_{0n}$ between the position of the stretching vibration $\bar{\nu}_{0n}$ and the position of the combination band $\bar{\nu}_{vib_{0n}+lib}$:

$$\bar{\nu}_{lib,0} = (\bar{\nu}_{vib_{0n}+lib} - \bar{\nu}_{0n})\left(\frac{\langle\psi_0|1/r^2|\psi_0\rangle}{\langle\psi_n|1/r^2|\psi_n\rangle}\right)^{1/2}. \tag{4}$$

Since OH and OD molecules should have nearly the same electronic structure the potential should be the same to a high order of approximation. Therefore, with the subscript I indicating values after isotopic substitution, the ratio of the direct librational wavenumbers $\bar{\nu}_{lib,n}$ ($n = 0$) and the corresponding value ($\bar{\nu}_{lib,n}$ ($n = 1, 2$)) derived from the difference of $\bar{\nu}_{0I}$ and the position of the combination band ($\bar{\nu}_{vib_{0n}+lib}$) is given by

$$\frac{\bar{\nu}_{lib,n}}{\bar{\nu}_{lib,n,I}} = \sqrt{\frac{J_I}{J}} = \sqrt{\frac{\mu_{m,I}}{\mu_m}\frac{\langle\psi_n|1/r^2|\psi_n\rangle}{\langle\psi_{n,I}|1/r^2|\psi_{n,I}\rangle}}. \tag{5}$$

3.2. OH/OD libration + vibration combination bands in ABO₃

The spectra of the fundamental OH stretching absorption at RT in several ABO₃ crystals are shown on the left of figure 1 together with the spectra of an absorption band discovered in the regoin of ~4450 cm⁻¹. The bandshape of this new absorption band is similar to
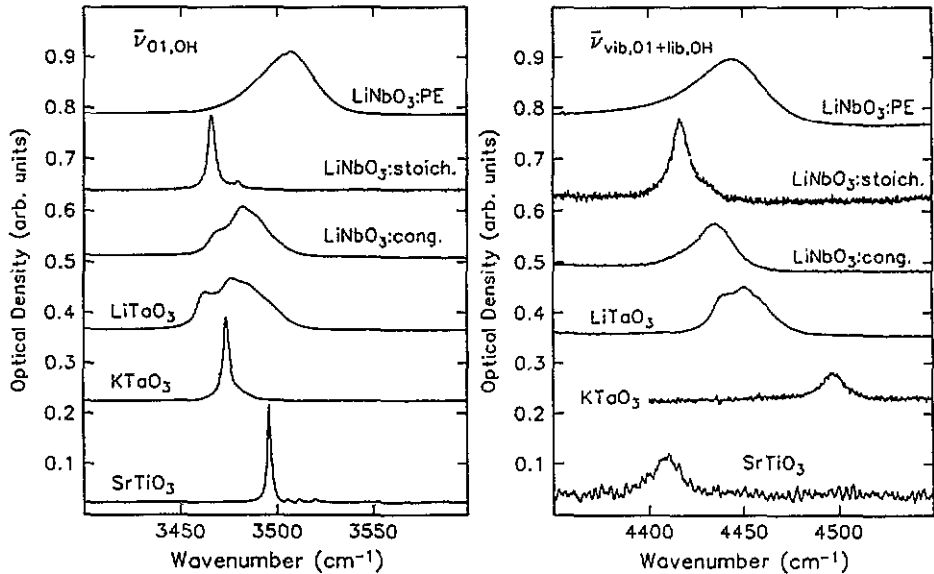
Figure 1. The OH stretching vibration $\bar{\nu}_{01,OH}$ (left) and the libration + vibration combination band $\bar{\nu}_{vib_{01}+lib,OH}$ (right) in different ABO$_3$ crystals at RT: in proton-exchanged LiNbO$_3$ (LiNbO$_3$:PE), in the bulk of nearly stoichiometric LiNbO$_3$ ((VTE) LiNbO$_3$:stoich.), in the bulk of congruent LiNbO$_3$ (LiNbO$_3$:cong.) and in the bulk of LiTaO$_3$, KTaO$_3$ and SrTiO$_3$ (LiNbO$_3$ and LiTaO$_3$: $E_{Light} \perp z \perp k_{Light}$). The spectra are shifted vertically for clarity.

the bandshape of the absorption band of the OH stretching vibration in the corresponding ABO$_3$ crystal, allowing us to ascribe this new absorption band to the same OH centres.

In crystals doped with deuterium a new analogous OD absorption band at ~ 3300 cm^{-1} can be found. To check that H$_2$ and D$_2$ are not responsible for this absorptions we prepared a crystal doped with both H and D, simultaneously. If H$_2$ and D$_2$ vibrations, respectively, were responsible for the new absorption band one would expect also to see a HD absorption band at ~ 3900 cm^{-1}. Figure 2 shows that no absorption band in this spectral range near ~ 3900 cm^{-1} could be found. Therefore H$_2$ or D$_2$ absorptions can be discounted.

Table 1. Observed wavenumbers of the peak positions of the absorption maxima of the OH and OD stretching vibrations ($\bar{\nu}_{01}$) and of the libration + vibration combination bands ($\bar{\nu}_{vib_{01}+lib}$) at RT.

	$\bar{\nu}_{01,OH}$ (cm^{-1})	$\bar{\nu}_{01,OD}$ (cm^{-1})	$\bar{\nu}_{vib_{01}+lib,OH}$ (cm^{-1})	$\bar{\nu}_{vib_{01}+lib,OD}$ (cm^{-1})
LiNbO$_3$:PE/DE	3508 ± 2	2588 ± 2	4444 ± 2	3278 ± 2
LiNbO$_3$:cong.	3484 ± 2	2574 ± 2	4436 ± 2	3274 ± 2
LiNbO$_3$:stoich.	3465.9 ± 0.2	2561.9 ± 0.1	4417 ± 1	3271 ± 1
LiTaO$_3$	3476 ± 2	2570 ± 2	4449 ± 2	3287 ± 2
SrTiO$_3$	3495.6 ± 0.1	2581.8 ± 0.1	4422 ± 1	3244 ± 1
KTaO$_3$	3473.8 ± 0.1	2565.9 ± 0.1	4498 ± 1	3297 ± 1

The peak positions of the vibrational absorption bands and of the libration + vibration combination bands in LiNbO$_3$, LiTaO$_3$, KTaO$_3$ and SrTiO$_3$ are listed in table 1. The wavenumbers of the difference $\bar{\nu}_{vib_{01}+lib} - \bar{\nu}_{01}$ for OH and OD in LiNbO$_3$:PE/DE show in a

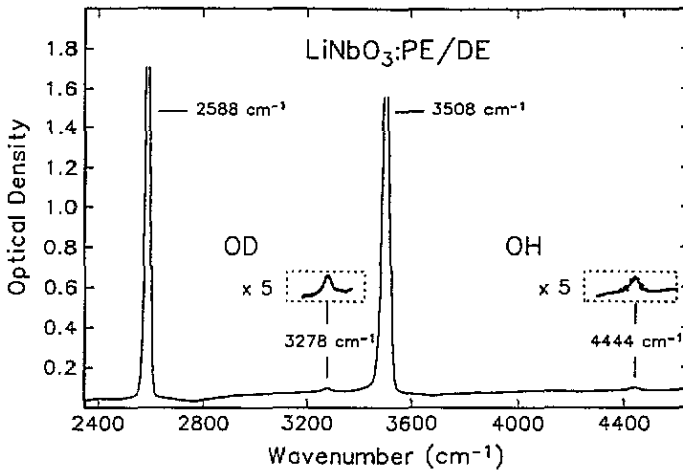**Figure 2.** The OH and OD stretching vibration ($\bar{\nu}_{01,OH} = 3508$ cm^{-1} and $\bar{\nu}_{01,OD} = 2588$ cm^{-1}) and OH and OD libration + vibration combination bands ($\bar{\nu}_{vib_{01}+lib,OH} = 4444$ cm^{-1} and $\bar{\nu}_{vib_{01}+lib,OD} = 3278$ cm^{-1}) in proton-exchanged (PE) and deuteron-exchanged (DE) LiNbO₃ (in the inset the spectra of the librational sidebands are enlarged by a factor 5). The optical densities of the OH and OD stretching vibration bands are so high that it is not possible to resolve them in this case. Therefore they are vertically limited. The spectra are recorded unpolarized for a z-cut crystal ($k_{Light} \parallel z$) at room temperature (RT).

first approximation the expected ratio after isotopic substitution according to equation (5):

$$\frac{\bar{\nu}_{vib_{01}+lib} - \bar{\nu}_{01}\ (OH)}{\bar{\nu}_{vib_{01}+lib} - \bar{\nu}_{01}\ (OD)} = \frac{936\ cm^{-1}}{690\ cm^{-1}} = 1.36 \pm 0.02.$$

This value can be compared with the value calculated according to equation (5):

$$\frac{\bar{\nu}_{vib_{01}+lib} - \bar{\nu}_{01}\ (OH)}{\bar{\nu}_{vib_{01}+lib} - \bar{\nu}_{01}\ (OD)} = \sqrt{\frac{\mu_{m,OD}}{\mu_{m,OH}} \frac{\langle\psi_{1,OH}|1/r^2|\psi_{1,OH}\rangle}{\langle\psi_{1,OD}|1/r^2|\psi_{1,OD}\rangle}} = 1.363 \pm 0.003.$$

This ratio was calculated using the free reduced mass μ_m of the OH (OD) oscillator and Morse-type wavefunctions [21] determined from the spectroscopic parameters of the OH oscillator in LiNbO₃:PE and of the OD oscillator in LiNbO₃:DE [22].

The agreement between these values indicates that a coupling of the OH oscillator via the oxygen atoms to the lattice plays only a minor role [23].

3.3. OH/OD libration + vibration combination bands in LiNbO₃

The properties of the OH and OD centres in LiNbO₃ deserve special attention. Normally LiNbO₃ crystals are available in the congruent composition, where the internal structural disorder leads to rather broad absorption bands ($\bar{\nu}_{max} = 3485$ cm^{-1}, $\Delta\bar{\nu} = 30$ cm^{-1} at RT).

Recently, stoichiometric LiNbO₃ prepared with the VTE technique has been shown to exhibit an OH absorption band which is one order of magnitude more narrow ($\bar{\nu}_{max} = 3466$ cm^{-1}, $\Delta\bar{\nu} = 3.3$ cm^{-1} at RT) than that of the congruent material [24].

However, the OH absorption bands after proton exchange in benzoic acid are equally broad ($\Delta\bar{\nu} = 30$ cm^{-1}) in both materials (congruent and stoichiometric)—both are situated at 3508 cm^{-1}.

We want to use these properties to study the indiffusion of protons from a proton-exchanged layer at the surface of stoichiometric (VTE) LiNbO₃ into the bulk of the crystal

after successive temperings in dry N_2 atmosphere at $T = 350\,°C$. The development of the vibrational and that of the combination band of the libration + vibration are of interest. Figure 2 shows the properties in the congruent material and figure 3 the variation of the OH absorption bands after successive temperings of the PE-treated stoichiometric (VTE) LiNbO$_3$.
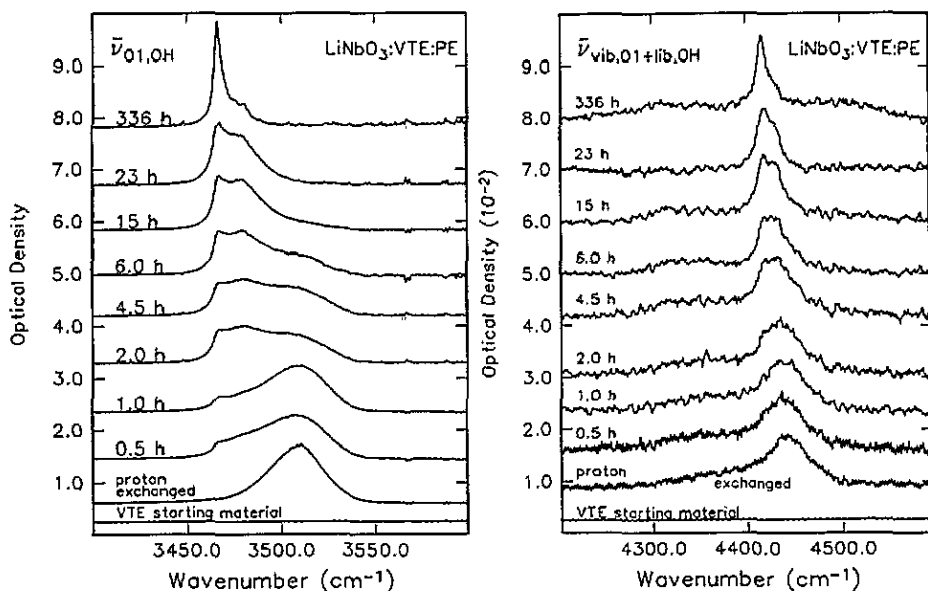

Figure 3. The OH vibration band $\bar{\nu}_{01,OH}$ (left) and libration + vibration combination band $\bar{\nu}_{vib_{01}+lib}$ (right) in proton-exchanged nearly stoichiometric (VTE) LiNbO$_3$ after successive temperings in dry N_2 atmosphere (350 °C). The tempering duration steps (in h) are indicated on the left of each spectrum. The spectra are recorded unpolarized, $k_{Light} \parallel z$, and are shifted vertically for clarity.

A thin nearly stoichiometric (VTE) LiNbO$_3$ x-cut probe, which shows no bulk OH absorption, was immersed in benzoic acid for 4 h. Then a broad ($\Delta \bar{\nu} \approx 30\ cm^{-1}$) OH absorption band with peak position at 3508 cm^{-1} caused by the OH absorption in the proton-exchanged layer could be observed (see the left of figure 3). After successive temperings in dry atmosphere (350 °C in N$_2$) the OH absorption in the exchanged layer decreases and two OH bulk absorption bands at 3481 cm^{-1} and 3466 cm^{-1} arise. After a final heat treatment, it is mainly the OH bulk absorption band in nearly stoichiometric (VTE) LiNbO$_3$ at 3466 cm^{-1} that remains.

The behaviour of the OH combination band $\bar{\nu}_{vib_{01}+lib}$ at $\bar{\nu}_{max} = 4444\ cm^{-1}$ in proton-exchanged nearly stoichiometric (VTE) LiNbO$_3$:PE is analogous. After successive temperings the peak position is lowered (shifting from 4444 cm^{-1} to 4417 cm^{-1}). Throughout, the bandshape of the libration + vibration combination band is similar to the bandshape of the OH stretching vibration.

The observed polarization dependence of these bands in LiNbO$_3$ and in the bulk of LiTaO$_3$ is listed in table 2 and will be discussed in section 3.5.

3.4. Concentration dependence of the OH libration + vibration combination band

In order to assign the new absorption bands to combination bands of libration + vibration we investigated their integral absorptions in the bulk of congruent and nearly stoichiometric

Table 2. The observed polarization dependence of the OH/OD vibrational mode $\bar{v}_{01,\text{OH/OD}}$ and of the libration+vibration combination band $\bar{v}_{\text{vib}_{01}+\text{lib}}$ in proton/deuteron-exchanged (PE/DE) LiNbO₃, in the bulk of nearly stoichiometric (stoich.) LiNbO₃, in the bulk of congruent (cong.) LiNbO₃ and in the bulk of LiTaO₃. The ratios for the absorption of light linearly polarized parallel and perpendicular to the z-axis ($I_\parallel/I_\perp$) are listed. The error is smaller than 0.05.

	Observed intensity ratio $I_\parallel/I_\perp$			
Crystal	$\bar{v}_{01,\text{OH}}$	$\bar{v}_{01,\text{OD}}$	$\bar{v}_{\text{vib}_{01}+\text{lib},\text{OH}}$	$\bar{v}_{\text{vib}_{01}+\text{lib},\text{OD}}$
LiNbO₃:PE/DE	0.03	0.02	0.50	0.80
LiNbO₃:cong.	0.03	0.02	0.58	0.75
LiNbO₃:stoich.	0.03	0.03	0.55	0.76
LiTaO₃	0.03	0.03	0.56	0.75

(VTE) LiNbO₃ as well as in the bulk of KTaO₃ as a function of the absorption coefficient of the fundamental OH stretching vibration $\bar{v}_{01}$ (as an indication of the OH concentration).

The OH libration + vibration combination band should exhibit a linear dependence on the OH concentration, and therefore a constant ratio of the integrated absorption of the stretching vibration I_{01} and the integrated absorption of the libration + vibration combination band $I_{\text{vib}_{01}+\text{lib}}$. In all the crystals investigated that are mentioned above the ratio $I_{01}/I_{\text{vib}_{01}+\text{lib}}$ was nearly constant, whereas the OH concentration varied by about an order of magnitude. This is shown in figure 4. Moreover this linear dependence also contradicts the interpretation of the new band as being due to a H₂ vibration, because there two protons are involved and for this case a quadratic concentration dependence is expected. Therefore the association of the new band with a combination of libration + vibration is justified.
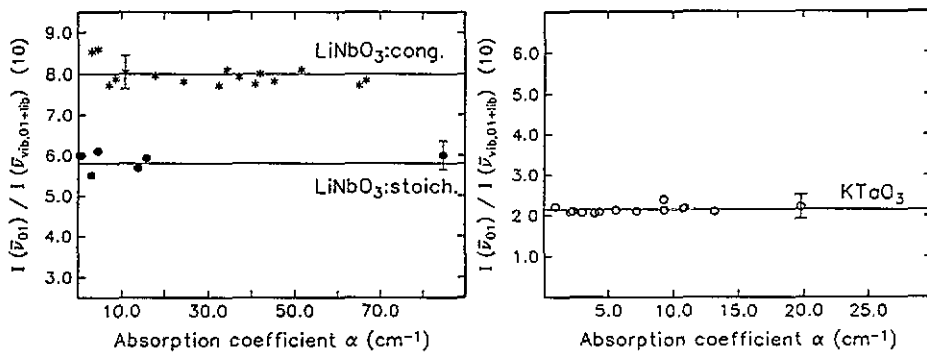

Figure 4. The integrated intensity ratio of the OH vibration band $\bar{v}_{01}$ and the OH libration + vibration combination band $\bar{v}_{\text{vib}_{01}+\text{lib}}$ in the bulk of congruent LiNbO₃ (*, left), in the bulk of nearly stoichiometric LiNbO₃ (•, left) and in the bulk of KTaO₃ (o, right) as a function of the absorption coefficient of the fundamental OH stretching absorption. The horizontal lines are guides for the eye.

3.5. Polarization dependence of the OH libration + vibration combination band

In LiNbO₃ and LiTaO₃ the OH/OD dipole vibrates in the plane perpendicular to z. In the case of incidence of linear polarized light, with k_{Light} perpendicular to z, and the polarization vector E_{Light} in general inclined at an angle θ with respect to the polar z-axis, the integrated absorption intensity I will be proportional to $\sin^2 \theta$.
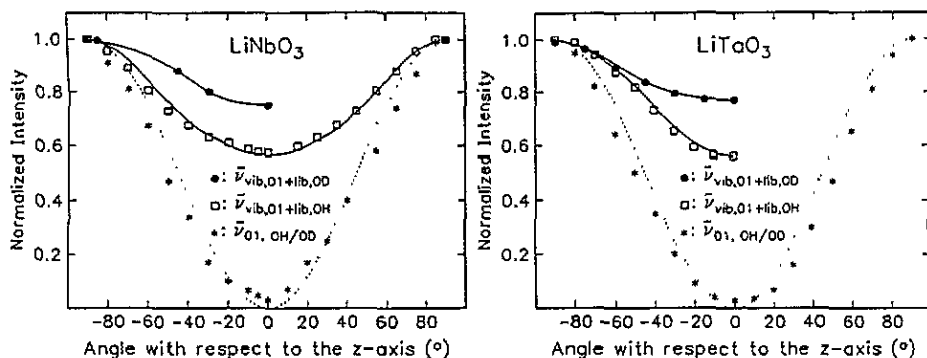
Figure 5. The polarization dependence of the OH/OD vibration band ($*: \bar{\nu}_{01,OH,OD}$), of the OH and the OD libration+vibration combination band ($\square: \bar{\nu}_{vib_{01}+lib,OH}$; $\bullet: \bar{\nu}_{vib_{01}+lib,OD}$) in the bulk of LiNbO$_3$ (left) and LiTaO$_3$ (right). The dotted lines show the expected dependence of the absorption for the OH/OD stretching vibration on the incidence of linear polarized light: $I(\theta) \sim \sin^2 \theta$ (for $k_{Light} \perp z$). The full lines are guides for the eye.

This behaviour is shown in figure 5 and follows within experimental error the predicted behaviour. The investigations of the libration + vibration combination bands in LiNbO$_3$ and LiTaO$_3$ exhibit, at the same spectral position for absorption parallel ($I_\parallel$) and absorption perpendicular ($I_\perp$) to z, a ratio of $I_\parallel/I_\perp \approx 0.55$ for OH and a ratio of $I_\parallel/I_\perp \approx 0.75$ for OD (see table 1). The observed intensity ratios $I_\parallel/I_\perp$ are listed in table 2. The libration + vibration combination bands show components of the dipole moment both parallel and perpendicular to z, revealing the three-dimensional and, in LiNbO$_3$ and in LiTaO$_3$ energetically isotropic character of the libration.

3.6. Combination of the libration with the second excited state of the vibration

If there exists a combination band composed of the libration with the fundamental stretching vibration, there should also exist a combination band composed of the libration with the second excited state of the vibration. We observed these libration + vibration combination bands $\bar{\nu}_{vib_{02}+lib}$ for the OH/OD oscillator in proton/deuteron-exchanged LiNbO$_3$:PE/DE with very high optical densities of the OH/OD stretching absorption. The spectra of the first overtone and the combination bands of the libration with the first overtone of the vibration are shown in figure 6.

In contrast to the OH and the OD librational combination bands that include the fundamental of the stretching vibration which have an integrated intensity ratio $I_\parallel/I_\perp(\bar{\nu}_{vib_{01}+lib}) < 1$, the librational combination bands that include the first overtone of the stretching vibration reveal an intensity ratio $I_{45°}/I_\perp(\bar{\nu}_{vib_{02}+lib}) > 1$ for OH and OD. For OD the ratio $I_{45°}/I_\perp(\bar{\nu}_{vib_{02}+lib})$ is of the order of ~ 2. Due to the small absorption intensity of the OH combination band $\bar{\nu}_{vib_{02}+lib}$ only a ratio $I_{45°}/I_\perp \geqslant 2$ can be estimated. Considering the experimental set-up employed, a ratio $I_\parallel/I_\perp(\bar{\nu}_{vib_{02}+lib}) \geqslant 3$ for OH and OD can be concluded. The different intensity ratios ($I_\parallel/I_\perp(\bar{\nu}_{vib_{01}+lib}) \approx 0.55$ for OD, $I_\parallel/I_\perp(\bar{\nu}_{vib_{01}+lib}) \approx 0.75$ for OH and $I_\parallel/I_\perp(\bar{\nu}_{vib_{02}+lib}) \geqslant 3$ for OH/OD) for the absorptions parallel and perpendicular to z support the identification of these new absorption bands as combination bands made up of the libration with the vibration because different overlap integrals of the wavefunctions of the librational and vibrational states involved can reveal different oscillator strengths for the absorptions parallel and perpendicular to the molecular axis of the OH/OD dipole.
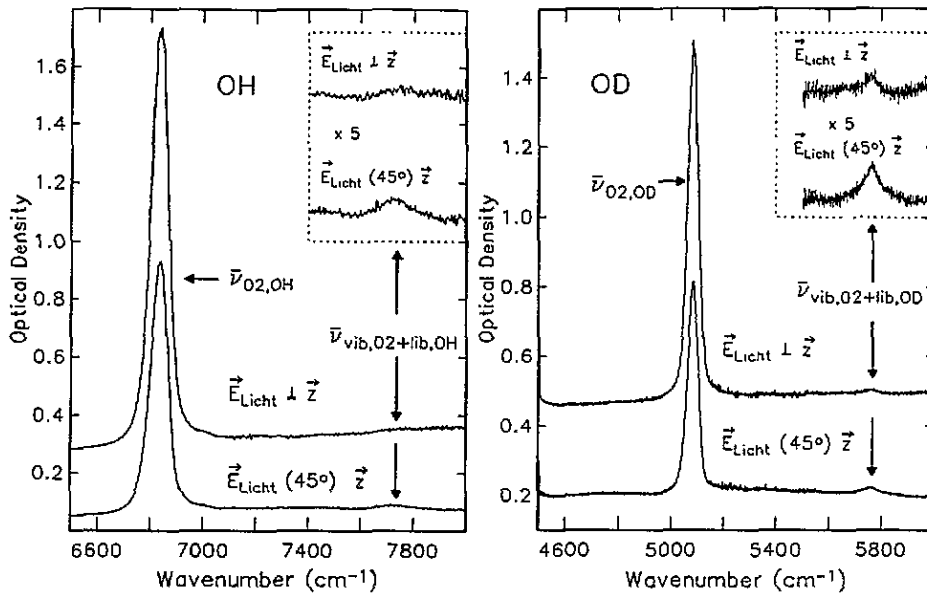
Figure 6. Absorption bands of the second excited state of the OH/OD stretching vibration ($\bar{\nu}_{02,OH/OD}$) at 6836/5084 cm^{-1} in LiNbO₃:PE/DE (for OH left and for OD right). The vertical arrows mark the OH/OD combination band that combines the libration with the second excited state of the vibration at $\bar{\nu}_{vib_{02}+lib} = 7738/5767$ cm^{-1}. In the inset the spectra of the combination bands $\bar{\nu}_{vib_{02}+lih}$ are enlarged by a factor 5. The k-vector of the incident lights inclined at an angle of 45° with respect to the z-axis. The light polarization is perpendicular to the z-axis (top) or has an angle of 45° with respect to the z-axis (bottom). The first overtones of the stretching vibration $\bar{\nu}_{02,OH}$ and $\bar{\nu}_{02,OD}$ show the ratio $I_{45°}/I_{\perp} = 0.5$ expected for this set-up. The spectra are recorded at RT.

Analogously to the method of calculation used in section 3.2 we investigate the ratios of the difference in wavenumbers of (i) the vibration and (ii) the librational combination band including the second excited state of the vibration of the OH/OD oscillator. The observed ratio of these differences

$$\frac{\bar{\nu}_{vib_{02}+lib} - \bar{\nu}_{02}\,(OH)}{\bar{\nu}_{vib_{02}+lib} - \bar{\nu}_{02}\,(OD)} = \frac{902\;cm^{-1}}{683\;cm^{-1}} = 1.32 \pm 0.03$$

can be compared with the ratio calculated according equation (5):

$$\frac{\bar{\nu}_{vib_{02}+lib} - \bar{\nu}_{02}\,(OH)}{\bar{\nu}_{vib_{02}+lib} - \bar{\nu}_{02}\,(OD)} = \sqrt{\frac{\mu_{m,OD}}{\mu_{m,OH}}\frac{\langle\psi_{2,OH}|1/r^2|\psi_{2,OH}\rangle}{\langle\psi_{2,OD}|1/r^2|\psi_{2,OD}\rangle}} = 1.356 \pm 0.004.$$

The calculated value of this ratio is in fact a little bigger than and beyond the error bars of the observed value, but here one has to take it into account that a simple harmonic oscillator model for the libration was used. With an expected librational anharmonic potential the librational states are lowered as compared with the energetic states of a harmonic librator. The energy lowering increases with increasing number of excited energy levels. In this case the calculated librational combination band position decreases in wavenumber. Moreover the equilibrium configuration of the OH/OD defect is determined by the charge distribution of the impurity and the surrounding ions of the host lattice. Therefore the lattice site of the OH/OD molecule does not necessarily correspond to the centre of mass of the impurity. In

this case the centre of mass may also librate and the moment of inertia increase resulting in a decreasing of the term under the square root.

4. Conclusions

The new absorption bands at about ~ 4450 cm^{-1} in $LiNbO_3$, $LiTaO_3$, $SrTiO_3$ and $KTaO_3$ can be identified as libration + vibration combination bands of the OH oscillator on the basis of the following experimental results.

The integrated absorption of the libration + vibration combination band $\bar{\nu}_{vib_{01}+lib}$ is found to vary linearly with the OH concentration in the bulk of nearly stoichiometric (VTE) $LiNbO_3$, congruent $LiNbO_3$ and $KTaO_3$.

Also a combination band of the libration combined with the second excited state of the vibration of the OH/OD oscillator in proton/deuteron-exchanged $LiNbO_3$ has been observed.

The isotope effect of the difference in wavenumbers of the vibration and the libration + vibration combination band shows the frequency ratio

$$\frac{\bar{\nu}_{vib_{0n}+lib} - \bar{\nu}_{0n} \, (\mathrm{OH})}{\bar{\nu}_{vib_{0n}+lib} - \bar{\nu}_{0n} \, (\mathrm{OD})} = \sqrt{\frac{\mu_{m,OD}}{\mu_{m,OH}} \frac{\langle \psi_{n,OH} | 1/r^2 | \psi_{n,OH} \rangle}{\langle \psi_{n,OD} | 1/r^2 | \psi_{n,OD} \rangle}}$$

expected for the OH $\leftrightarrow$ OD substitution assuming, in a first approximation, a nearly harmonic potential for the librational mode.

The observed wavenumber differences of the OH and OD libration + vibration combination band from the fundamental stretching vibration ($\bar{\nu}_{vib_{01}+lib} - \bar{\nu}_{01}$) and the corresponding one of the libration + vibration combination band from the second excited state of the vibration ($\bar{\nu}_{vib_{01}+lib} - \bar{\nu}_{02}$) can be explained roughly using a simple harmonic oscillator model for the librational motion.

The librational combination bands exhibit absorption parallel and perpendicular to z at the same frequency, indicating the three-dimensional and energetically isotropic character of the libration in $LiNbO_3$ and in $LiTaO_3$.

The energies of the libration + vibration combination bands are the same for the absorption parallel and perpendicular to z. This is as expected, due to the isotropic activation energy of the protonic conductivity in $LiNbO_3$ involving the librational motion as the attempt frequency.

Further effort will be devoted to observing the direct OH libration in $LiNbO_3$ and $LiTaO_3$ containing high OH concentrations (due to proton exchange) by Raman spectroscopy.

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