Raman and FTIR study of NaOH and NaOD under pressure

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Abstract. The effect of pressure on the Raman and IR modes of NaOH and NaOD have been measured for pressures up to 25 GPa and temperatures down to 100 K, using the diamond anvil technique. Changes in the Raman and IR spectra indicate transformations into different structures. The results reveal that the phase diagrams of NaOH and NaOD are very similar and show only small differences in the respective transition pressures.

1. Introduction

All alkali metal hydroxides MOH and MOD exhibit polymorphism at ambient pressure. At low temperatures, the heavy homologes (M = K, Rb, Cs) adopt structures with hydrogen bonding [1] while for the light homologues (M = Li, Na), except NaOD, hydrogen bonding is absent [2, 3].

High-pressure studies have been reported for LiOH and NaOH [2, 4] and for a high-pressure modification of LiOH hydrogen bonding was suggested [2]. In this study we report on the behaviour of NaOH and NaOD at high pressure and interpret the Raman and IR spectra with respect to hydrogen bonding.

Below its melting point NaOH has the cubic rocksalt structure (I), in which the $(OH)^-$ ion shows quasifree rotation or, in a different model, there is a rapid reorientation between preferred orientations of the molecule [5]. At 566 K NaOH transforms into a monoclinic structure (II), in which the protons become localized. At 514 K another transformation into the orthorhombic low-temperature structure (III) is well established [3].

NaOD shows the same sequence of phases when the temperature is lowered from the melting point to room temperature [3]. At 160 K, however, it transforms into an additional monoclinic structure (IV) with hydrogen bonded zigzag chains. This structure is stable down to liquid-He temperature [6, 7].

High-pressure DTA and piston displacement measurements on NaOH provided information about two new high-pressure phases with, as yet, unknown structures. At room temperature one of these phase transitions (III–V) occurs at 0.84 GPa with a $7 \cdot 8\%$ volume change [4].

2. Experimental technique

The present high-pressure experiments were performed in gasketed diamond anvil cells. Low-fluorescence diamonds were used in the Raman cell [8] and type IIa

diamonds in the IR cell [9]. Inconel gaskets of about 50 μm thickness with initial hole diameters of 180 μm (Raman) and 300 μm (IR) were used. Pressures were determined from the red shift of the ruby fluorescence, using the linear ruby scale with $dr/dP = 0.132$ cm^{-1} GPa^{-1} [10].

NaOH (semiconductor grade pallets, Aldrich Chemicals) was dehydrated in a vacuum. NaOD was prepared from a 40 wt% solution of NaOD in D_2O (99.8% D, Aldrich Chemicals). The samples were loaded into the cells at liquid-N_2 temperature under a dry nitrogen atmosphere. In some of the Raman experiments, N_2 was used as a pressure transmitting medium.

The Raman spectra were excited with the 514.5 nm line of an Ar$^+$ ion laser. The backscattered light was analysed using a Spex 1402 Double Spectrometer with a spectral resolution of 3 cm^{-1}. The light intensity was detected by a cooled photo-multiplier, coupled to a photon counting system. In the Bruker IFS 113v Fourier Spectrometer for the IR measurements, a tungsten halogen lamp was used together with a Si:CaF$_2$ beamsplitter. The signal was detected by a liquid-N_2 cooled InSb detector. The spectral resolution was 8 cm^{-1}.

In transmission measurements with a diamond anvil cell, the spectra are obscured between 1800 cm^{-1} and 3800 cm^{-1} by the two- and three-phonon absorption of the diamonds [11]. This effect influences particularly the fundamental line of the IR-active OD stretch mode. In addition, the spectra are distorted by multi-reflection between the two parallel diamond–sample interfaces, especially if the two refractive indices differ considerably. At higher pressures, when the refractive indices of the sample and the diamond anvils become comparable and the diamond surfaces start to get curved, this effect is less pronounced.

3. Results

3.1. Raman and IR spectra at room temperature

For the room temperature structure III with symmetry D_{2h}, the reducible representation of the zone centre modes decays into six different types of irreducible representations:

$$\Gamma = 3A_g + 3B_{2g} + 3B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$$

whereby the nine g-modes are Raman-, and the six u-modes are IR-active. Because of the small hydrogen mass, the H or D motions may be regarded as uncoupled with respect to the motions of the heavier constituents in a first approximation. There are two different frequency ranges in which lines are to be expected. For both Raman and IR measurements, there is one mode, respectively, which is mainly of H or D stretching type. All the other modes should have frequencies below 1000 cm^{-1}. Two Raman- and two IR-active modes have mainly H or D librational character, and the remaining modes belong to translational and librational motions of the heavier constituents.

At room temperature, the transformation into the high-pressure phase V can easily be detected in the Raman spectra of the stretch modes: figure 1 shows that the single line in NaOH and NaOD shifts first to lower wavenumbers, accompanied by an increasing linewidth. At the transition, a new line appears about 50 cm^{-1} below the initial value. Its intensity increases at the expense of the intensity of the initial
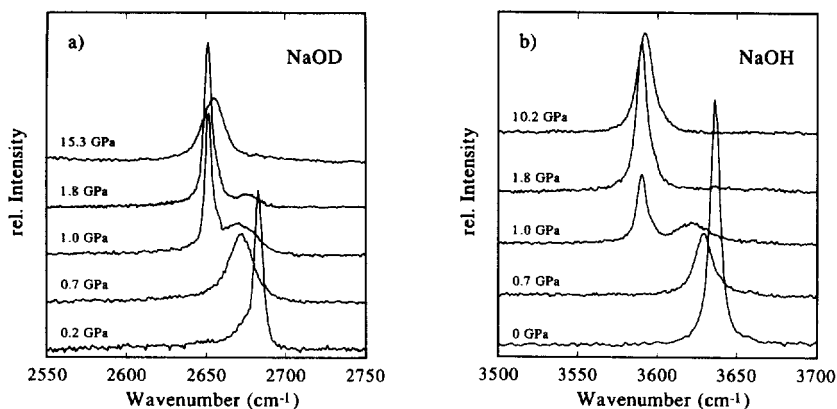
Figure 1. Raman spectra of the stretch modes in NaOD (*a*) and NaOH (*b*) at room temperature and different pressures.
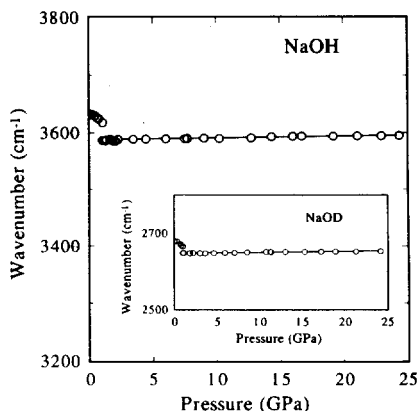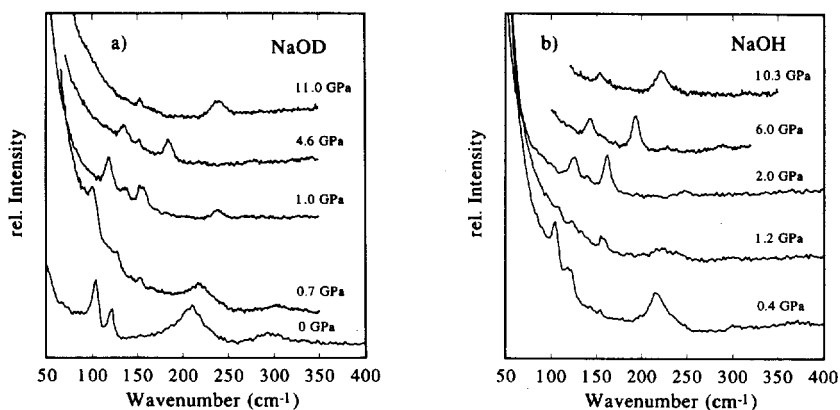

Figure 2. Effect of pressure on the Raman-active stretch modes at room temperature.

line. Thus, spectra showing both lines are assumed to be caused by a phase mixture. In the high-pressure phase V, the new line has a slight positive pressure dependence (figure 2).

This high-pressure phase transition (III–V) shows up also in the low-frequency Raman spectra (figure 3; for spectra at ambient pressure see figure 7). Three new lines appear and increase in intensity at the expense of the original four bands until only the new bands are present at about 2 GPa. A region of intergrowth is again observed. At pressures above 10 GPa, only one line can be detected while the others have disappeared into the background. The pressure dependence of the line frequencies is shown in figure 4, and table 1 gives the results of linear fits to the data together with the linear coefficients of the stretch modes.

As nothing is known about the structure of the high-pressure phase, a mode assignment can only be tentative. However, for the observed lines, the absence of an isotope shift indicates a translational or librational character of the modes, related to the motions of the rigid molecular units. The small number of observed lines is an indication that the number of formular units per primitive unit cell is conserved.

The differences in the spectra for phase III and the high-pressure phase V are more significant in the IR spectra than in the Raman spectra (figure 5). Here again,

Figure 3. Raman spectra of NaOD (*a*) and NaOH (*b*) in the low-frequency range at room temperature and different pressures.
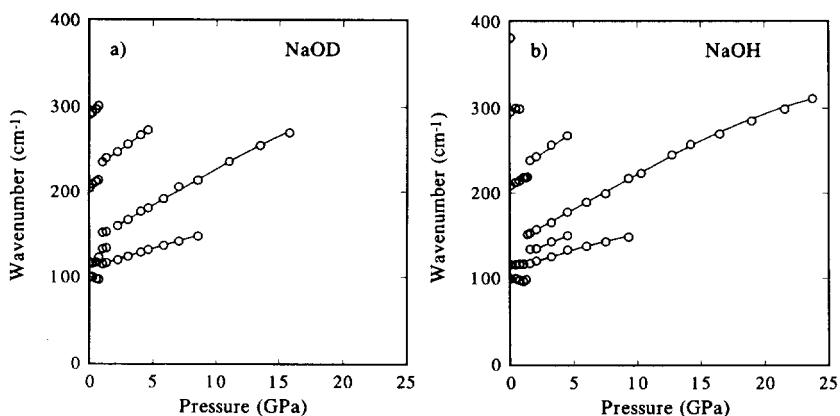
Figure 4. Effect of pressure on the low-frequency Raman modes of NaOD (*a*) and NaOH (*b*) at room temperature.

Table 1. Linear relations describing the effect of pressure on the Raman frequencies in phase V.

$E(P) = E_0 + E'P$			
NaOD		NaOH	
E_0 (cm^{-1})	E' (cm^{-1} GPa^{-1})	E_0 (cm^{-1})	E' (cm^{-1} GPa^{-1})
2647.2(3)	0.24(2)	3587.0(4)	0.36(3)
225.1(9)	10.4(3)	223.9(18)	9.9(7)
143.7(13)	8.22(14)	139.8(7)	8.2(8)
110.9(4)	4.44(8)	112.7(13)	4.0(2)

however, the spectra for NaOD are very similar to the NaOH spectra. In the region of the IR-active stretch mode, essentially only one band can be observed for phase III, and its frequency differs only slightly from the respective Raman band. As in

the Raman spectra, the phase transition is indicated by the appearance of a new band. However, in addition four new bands can be observed in the overtone region, which can be assigned to combinations of the stretch mode with translational and librational modes. Because of its isotope shift, especially the overtone with the highest frequency can be assigned to a combination with a H or D libration. Figure 6 shows the variations of the observed lines with pressure, and table 2 gives the results of linear fits to the data.
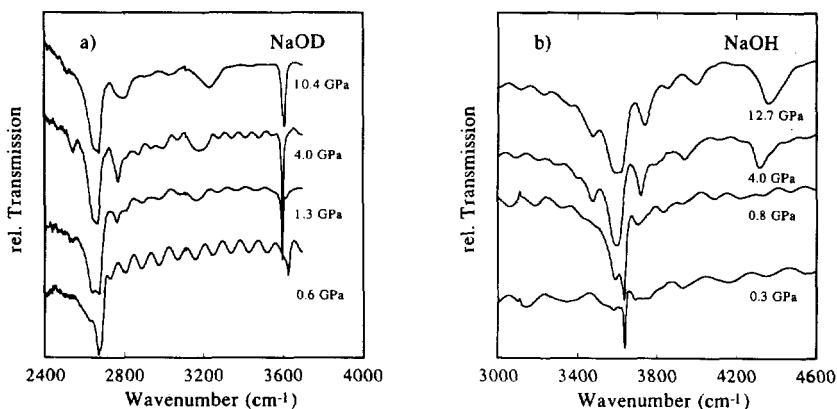

Figure 5. IR spectra of the stretch and combination modes in NaOD (*a*) and NaOH (*b*) at room temperature and different pressures.
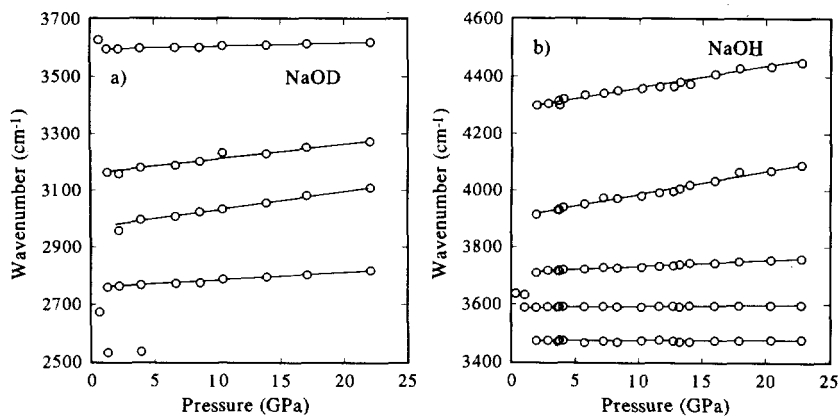

Figure 6. Effect of pressure on the IR-active stretch and combination modes in NaOD (*a*) and NaOH (*b*) at room temperature.

The appearance of overtones in the IR spectra of the high-pressure phase may be an indication of a strong increase in anharmonic contributions to the intramolecular forces. However, also deviatoric stresses in the samples under non-hydrostatic conditions in the diamond anvil cell may be responsible in part for the coupling of these modes.

Table 2. Linear relations describing the effect of pressure on the IR frequencies in phase V.

$E(P) = E_0 + E'P$			
NaOD		NaOH	
E_0	E'	E_0	E'
(cm^{-1})	$(\text{cm}^{-1}\ \text{GPa}^{-1})$	(cm^{-1})	$(\text{cm}^{-1}\ \text{GPa}^{-1})$
3593.7(7)[a]	1.18(5)[a]		
3155(6)	5.6(5)	4286(3)	7.4(3)
2956(8)	7.5(8)	3902(3)	8.3(3)
2755.2(16)	2.80(13)	3709.1(11)	2.26(9)
—[b]	—[b]	3589.3(5)	0.37(4)

[a] H-impurity.
[b] Fundamental band obscured by diamond absorption.

### 3.2. Raman spectra at low temperatures

Figure 7 shows Raman spectra of NaOD and NaOH at ambient pressure (room temperature and 110 K, respectively). For NaOD the line of the stretch mode splits at the transformation temperature to the hydrogen bonded phase IV, accompanied by a small jump to lower wavenumbers, clearly different from the behaviour of the single line of NaOH, which shows only a small shift to higher wavenumbers with decreasing temperature.
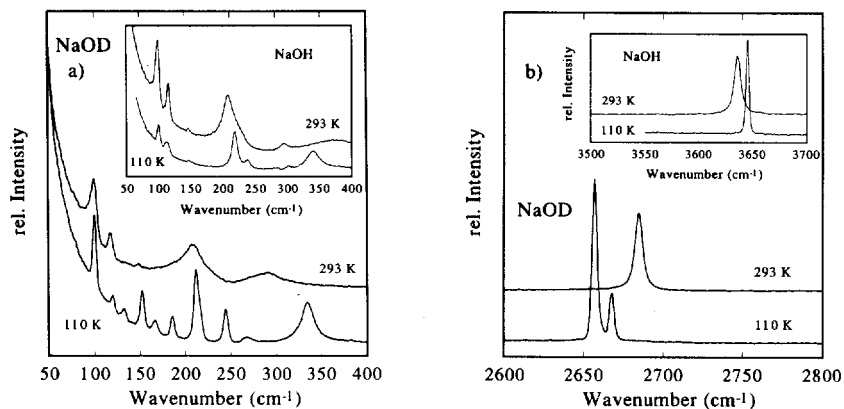
Figure 7. Raman spectra (ambient pressure) at room temperature and at 110 K in the low-frequency range (*a*) and of the stretch modes (*b*) in NaOD and NaOH (inserts).

The Raman spectra in the low-frequency region are also considerably different for the two structures. For NaOD the doubling of the unit cell shows up in a splitting of most of the lattice modes.

Raman spectra for NaOH have been reported previously [12, 13], and also for NaOD [13]. The present spectra for NaOH are in good agreement with the reported results. However, due to the higher signal-to-noise ratio in the present experiments, the III–V transformation in NaOD shows up in the present Raman spectra, in contrast to the previous results [13].

At sufficiently low temperatures, the results for isothermal compression are different from those at room temperature. Figure 8 shows Raman spectra at 200 K and increasing pressures for the stretch modes. The single lines split in an intermediate pressure range and show a strong decrease in frequency with increasing pressure, before a new line appears, which is characteristic of the high-pressure phase. Figure 9 shows the effect of pressure on the observed Raman lines at 110 K.
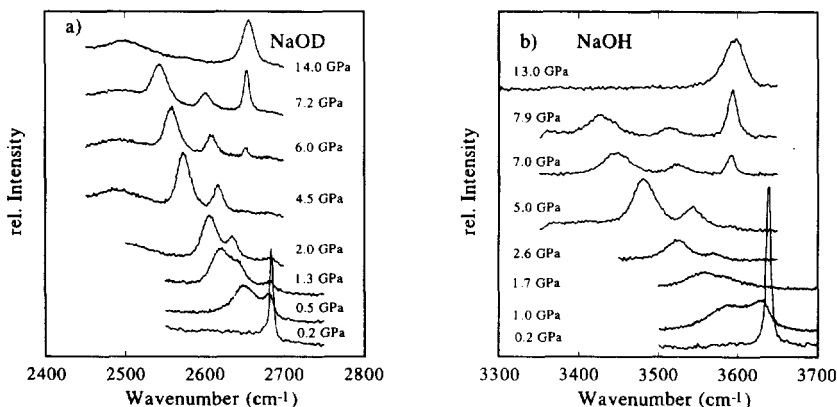
Figure 8. Raman spectra of NaOD (*a*) and NaOH (*b*) of the stretch modes at 200 K and different pressures.
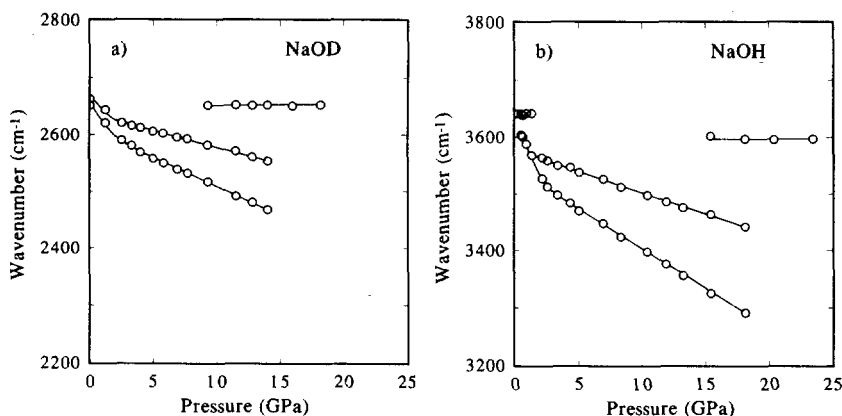
Figure 9. Effect of pressure on the stretch modes in NaOD (*a*) and NaOH (*b*) at 110 K.

On isothermal decompression the high-pressure phase V remains metastable over a large range in pressure for both NaOH and NaOD. At sufficiently low temperatures, both substances can be kept in phase V even down to ambient pressure. At higher temperatures the transformation into phase III can be observed below 1 GPa. Table 3 gives the observed transformation pressures for isothermal compression and decompression.

Table 3. Transformation pressures at different temperatures.

		Compression		Decompression
	T (K)	P (GPa)	P (GPa)	P (GPa)
NaOH	293	1 [a]		0.8 [d]
	250	1 [b]	3.2... 5.8 [c]	0.5 [d]
	200	0.9 [b]	6.0...12.0 [c]	
	160	0.8 [b]	7.8...14.8 [c]	
	110	0.6 [b]	10.4...23.0 [c]	
NaOD	293	1 [a]		0.8 [d]
	250	0.9 [b]	3.2... 7.0 [c]	0.5 [d]
	200	0.5 [b]	5.1...10.1 [c]	
	160		6.8...12.8 [c]	
	110		8.6...18.9 [c]	

[a] Transition from phase III into phase V.
[b] Transition from phase III into phase IV.
[c] Onset and completion of the transition from phase IV into phase V.
[d] Reverse transition from phase V into phase III.

4. Discussion

It is commonly accepted that a negative pressure shift of an OH stretch mode is a good indicator of the presence of hydrogen bonding [14]. From the strong decrease of the stretch frequencies in phase IV (figure 9), the presence of hydrogen bonds can thus be claimed for NaOH and NaOD in this phase.

In phase V the stretch frequency remains nearly unchanged over an extended pressure range (figure 9), indicating the absence of linear hydrogen bonds. However, bent [15] or bifurcated [16] hydrogen bonds can exhibit only weak pressure dependences, and thus cannot be excluded.

In the vicinity of the III–V phase transition at low pressures, the stretch modes exhibit a negative pressure shift, accompanied by a broadening of the respective lines (figure 1 and figure 2). At first, this appears to be an indication of the presence of hydrogen bonds in NaOH and NaOD under ambient conditions. However, crystal instabilities as a precursor of the phase transitions, accompanied by a strong increase of anharmonic interatomic interactions, are more likely to be responsible for the observed pressure shift.

The information on structural stabilities and metastabilities for the phases III, IV, and V, obtained from the present Raman and FTIR studies on both NaOH and NaOD under pressure and low temperatures are illustrated in figures 10 and 11 (regions of metastabilities are represented by shading). The increasing sluggishness of the transition from phase IV to V at low temperatures is also shown by the dark portions in the arrows pointing to the right. These portions represent qualitatively the amount of retained phase IV in a series of isothermal measurements with step-wise increasing pressure. Similar isothermal measurements with stepwise decreasing pressure reveal complete quenchability of phase V down to ambient pressure, as long as the temperature remains below 200 K, illustrated by open arrows pointing to the left at ambient pressure. Partial backtransformation of phase V directly to phase III is, however, noticed at temperatures above 200 K in both NaOH and NaOD, and

the transition between phase III and IV seems to reveal much smaller hysteresis, as indicated by the half-filled Ds. Thus, by taking reasonable average values between the upward and downward transformation ranges, one can derive rough estimates for the (equilibrium) transition pressures as shown by the broken lines in figures 10 and 11 for the transitions between the phases III and IV, as well as IV and V.
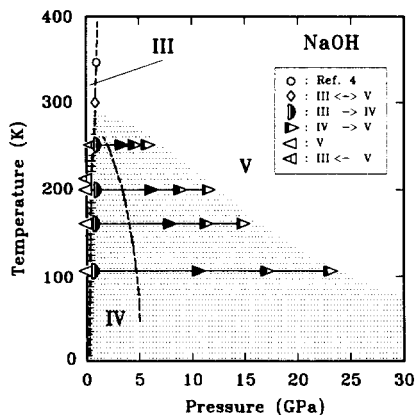

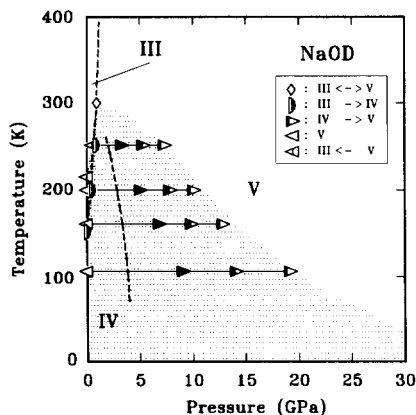**Figure 10.** Tentative phase diagram of NaOH (see text).

Figure 11. Tentative phase diagram of NaOD (see text).

From a comparison of figures 10 and 11, one can see that the difference in these two phase diagrams is only marginal, and basically, a shift in the pressure scale of NaOD by less than 1 GPa to higher pressures on the NaOH pressure scale generates a perfect match in both diagrams. Thus, the difference in the structural sequences of NaOH and NaOD at ambient pressure are almost fortuitous.

5. Conclusions

We summarize the present results as follows:

(1) The transformation into the high-pressure phase V in NaOH and NaOD shows up in changes of the Raman and IR spectra. The small positive shifts of the stretch modes indicate the absence of linear hydrogen bonds in this phase.

(2) The Raman spectra at ambient pressure and low temperatures for NaOH and NaOD differ considerably according to the different structures.

(3) On isothermal compression at low temperatures, the Raman spectra reveal the formation of hydrogen bonds also for NaOH.

(4) Upon further compression both substances transform into the high-pressure phase V also at low temperatures. At sufficiently low temperatures, this phase can be retained down to ambient pressure.

(5) The phase diagrams of NaOH and NaOD at low temperatures are very similar and show only small differences in the respective transition pressures.

Acknowledgments

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