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Vibrational spectroscopy at high pressures†—an infrared and Raman study of lithium hydroxide monohydrate: hydrogen bond formation at high pressures

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Abstract. Changes in the infrared and Raman spectra of lithium hydroxide monohydrate indicate that a phase transition occurs at close to 90 kbar upon compression. In particular, there is a doubling of the vibrations associated with the hydroxyl ion and a change in sign of the $d\nu/dp$ values for the hydroxyl O–H stretches from positive to negative. These results indicate that the transition involves the formation of weak hydrogen bonds, in which the hydroxyl hydrogens taken part, and the doubling of the size of the primitive unit cell. A large hysteresis was observed with the reverse transition occurring near 33 kbar.

1. Introduction

We have shown recently that lithium hydroxide, in which hydrogen bonding is absent under ambient conditions, undergoes a phase transition at high pressure involving the formation of hydrogen-bonded chains [1]. In the monohydrate, while there are hydrogen bonds between the water molecules and the hydroxyl oxygen, the hydroxyl hydrogen is not involved in a hydrogen bond. The monohydrate has a monoclinic structure, space group $C2/m$ (C_{2h}^3) with $z = 4$ [2–6] (figures 1 and 2), in which lithium is surrounded tetrahedrally by two hydroxyl and two water oxygens. The Li atoms and hydroxyl oxygens line in the ab plane and form four-membered rings. These rings are connected through water molecules to form infinite double chains running along c , which are in turn linked together by the hydrogen bonds between the water molecules and the hydroxide ions.

The present study was undertaken in order to determine whether a hydrate with a structure that is rather more complex than the parent hydroxide would also undergo a transition involving the formation of hydrogen bonds.

2. Experimental details

$\text{LiOH} \cdot \text{H}_2\text{O}$ (Fluka Chemie AG, purity 99.5%+) was used without further purification and was loaded into the diamond anvil cell (DAC) along with a ruby chip or a layer of

† This paper is part 59 in our series on vibrational spectroscopy at high pressures. Part 58 is Adams D M and Haines J 1991 *J. Phys. Chem.* **95** 7068.

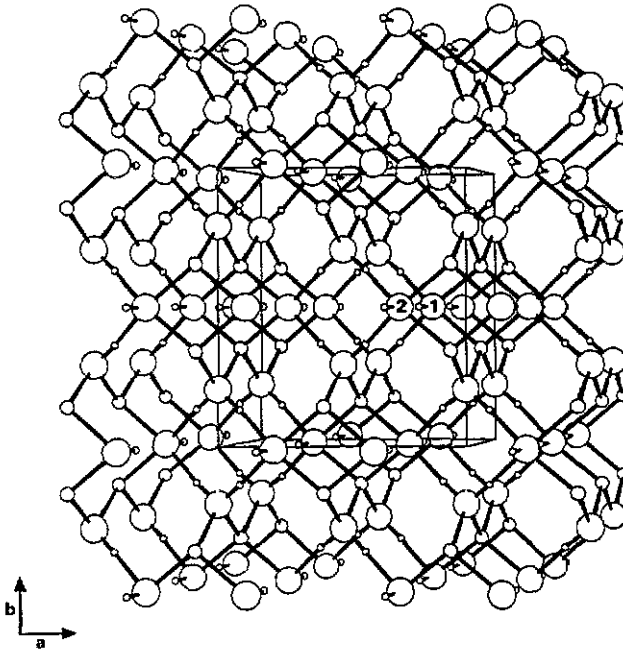


Figure 1. The structure of lithium hydroxide monohydrate.

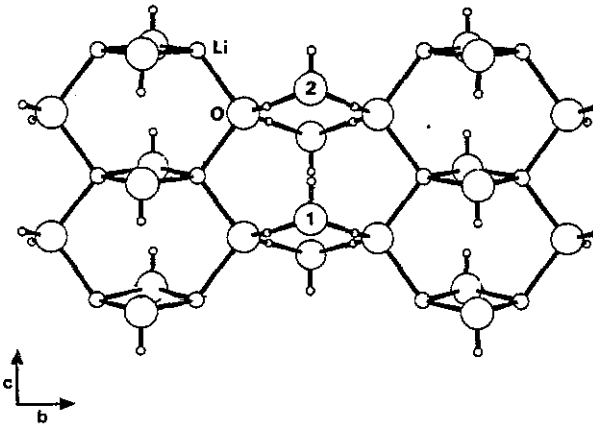


Figure 2. Structural detail of $\text{LiOH} \cdot \text{H}_2\text{O}$: phase I showing the double chains.

0.21% w/w NaNO_3 in NaBr as a pressure calibrant [7, 8] for the Raman and infrared experiments, respectively. Stainless steel gaskets of varying thicknesses with an initial hole diameter of $400 \mu\text{m}$ were used to contain the sample and calibrant. There was evidence of non-hydrostatic conditions in the Raman experiment, and therefore a second run using Nujol as a pressure-transmitting fluid was performed. Agreement was observed between the two runs up to 60 kbar, above which only the results of the Nujol run are reported.

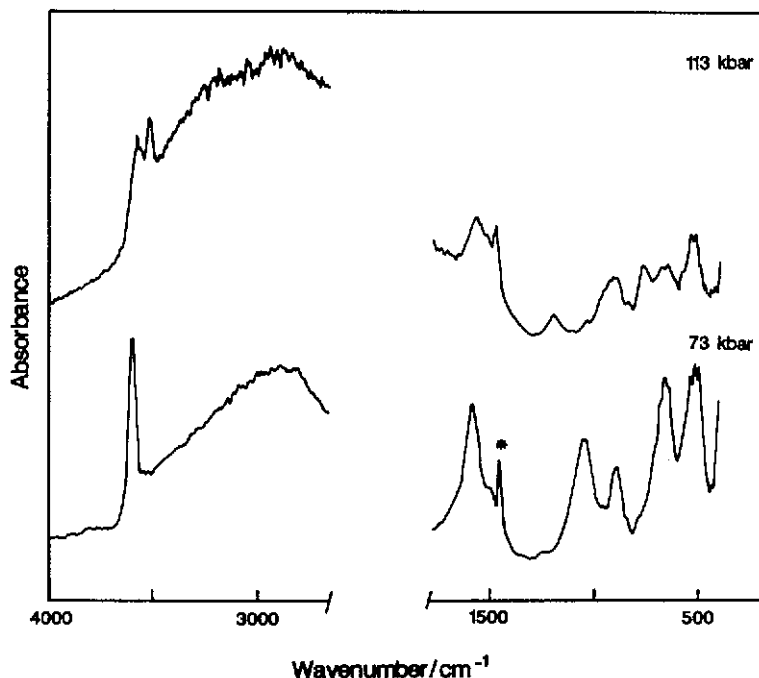


Figure 3. Infrared spectra of $\text{LiOH} \cdot \text{H}_2\text{O}$: phase I at 73 kbar and phase II at 113 kbar (* = ν_3 of NO_3^-).

Raman spectra were obtained in back-scattering configuration using a Coderg T800 spectrometer. A Spectra Physics Model 164 argon ion laser (488.0 nm line) was used for excitation. Infrared spectra were acquired on a Bio-Rad Digilab FTS-40 spectrometer. The Raman and infrared spectra were obtained at 18 and 31 °C, respectively.

3. Results

Factor group analysis [9, 10] predicts that $\text{LiOH} \cdot \text{H}_2\text{O}$ will have 15 infrared-active and 18 Raman-active vibrations. Of these, 10 were observed in the mid-IR spectrum and 10 in the Raman spectrum of $\text{LiOH} \cdot \text{H}_2\text{O}$ in the DAC. Several Raman bands were, however, too weak to follow at high pressure. All the vibrations hardened with increasing pressure (table 1) except for the broad water O–H stretches in the 3400–2600 cm^{-1} region which were found not to shift within experimental error. It is possible, however, that these bands soften due to an increase in the strength of the H bonds between the water molecules and the hydroxyl ions and that the shift in wavenumber was small compared to the linewidth of these bands and hence not observed. The hardening of the hydroxyl O–H stretch confirms that the hydroxyl hydrogen is not hydrogen bonded. Apart from the broadening of many bands, in particular, the H_2O librations and the Li–O lattice modes in the 700–600 cm^{-1} and 500–400 cm^{-1} regions respectively, no further changes were observed below 90 kbar.

At this pressure, the hydroxyl O–H stretch was found to split into two components in both the IR and Raman spectra and two new bands were observed at 1179 and 759 cm^{-1}

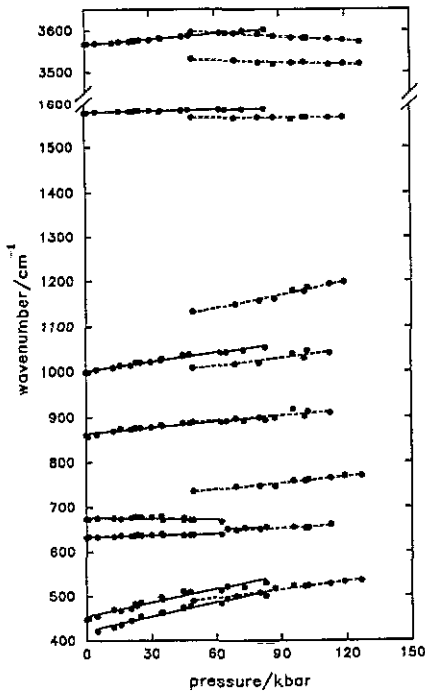


Figure 4. Pressure dependence of selected infrared modes of $\text{LiOH} \cdot \text{H}_2\text{O}$ in phase I (solid lines) and phase II (dashed lines).

in the infrared spectrum (figures 3–5). The 1179 cm^{-1} band can be attributed to a libration of the hydroxyl ion, while the 759 cm^{-1} band could be either a hydroxyl or a water libration. It should be noted that the 994 cm^{-1} band in the low-pressure phase, phase I, has been assigned to the hydroxyl librations [9, 10], which are accidentally degenerate as a result of the centre of mass of the hydroxyl ion being so close to the oxygen atom. If the hydroxyl hydrogens were to become involved in hydrogen bonds, this degeneracy would be lifted and significant shifts in frequency would be expected relative to that of the original band. It is therefore difficult to assign the 759 cm^{-1} band with confidence. The infrared and Raman components of the hydroxyl O–H stretches were separated by more than 15 cm^{-1} (table 1) indicating that mutual exclusion applies and therefore that the new structure is centrosymmetric. This and the splitting and appearance of new bands require that the primitive unit cell doubles in size. Several discontinuous changes in frequency were also observed. In particular, $\nu_{\text{as}}(\text{H}_2\text{O})$ at 3070 cm^{-1} exhibited an increase in frequency of more than 100 cm^{-1} , while $\delta(\text{H}_2\text{O})$ at 1588 cm^{-1} exhibited a decrease of close to 20 cm^{-1} . This indicates a weakening of the hydrogen bonds between the water molecules and the hydroxyl ion. Such a weakening of the hydrogen bonds at the phase transition is reminiscent of what is observed at the high-pressure phase transitions in H_2O ice [11].

The most significant changes in slope on the wavenumber versus pressure plots (figures 4 and 5) were observed for the hydroxyl O–H stretches, for which the $d\nu/dp$ values changed in sign from positive to negative (table 1). A negative pressure dependence is commonly observed for hydroxyl stretching frequencies in situations

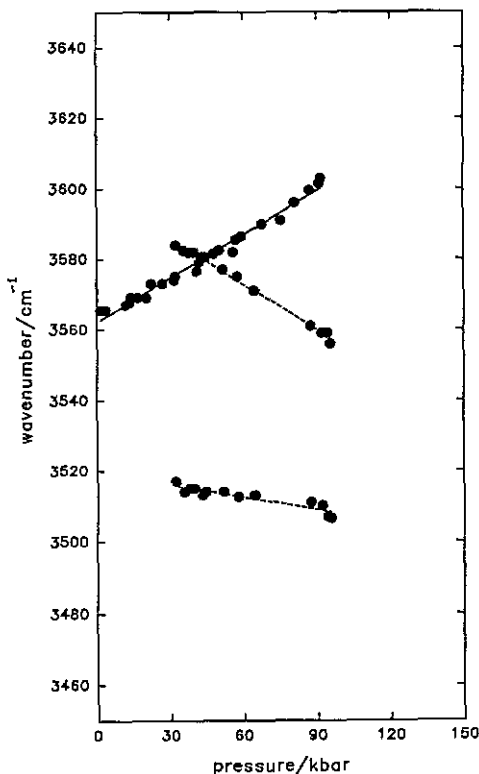


Figure 5. Pressure dependence of the Raman-active hydroxyl stretches of $\text{LiOH} \cdot \text{H}_2\text{O}$ in phase I (solid line) and phase II (dashed lines).

where hydrogen bonding occurs; therefore the present result is consistent with the formation of weak H bonds involving the hydroxyl hydrogens.

The Li–O lattice modes showed little change at the phase transition which would imply that the lithium–oxygen portion of the structure is relatively unaffected by the transition.

Upon decompression, a large hysteresis was observed with the reverse transition beginning at close to 33 kbar. This is characteristic of a transition that is strongly first order.

4. Discussion

The results indicate that the phase transition primarily involves a change in the hydrogen bonding environment about the hydroxyl anion in the $[(\text{OH})_2(\text{H}_2\text{O})_2]$ units which link the double chains (figure 2). Specifically there is formation of weak hydrogen bonds through the hydroxyl hydrogen and a slight weakening of the water–hydroxyl H bond. The magnitude of the splitting of the hydroxyl stretch would imply that the hydroxyl stretches in phase II are strongly coupled. Strong coupling between hydroxyl ions is most likely to occur if they are directly hydrogen bonded to one another. In the parent structure, under ambient conditions, the shortest hydroxyl O–O distance is 0.3195 nm,

Table 1. Vibrational data for lithium hydroxide monohydrate.

Phase I					Phase II				
ν_{IR} (cm^{-1}) (25 kbar)	ν_{Raman} (cm^{-1}) (27 kbar)	$d\nu/dp$ (cm^{-1} kbar $^{-1}$)	ν_0^\dagger (cm^{-1})	ν_{IR} (cm^{-1}) (95 kbar)	ν_{Raman} (cm^{-1}) (94 kbar)	$d\nu/dp$ (cm^{-1} kbar $^{-1}$)	ν_0^\dagger (cm^{-1})		
3576		0.44	3566	3583		-0.31	3613		
	3573	0.44	3561	3522		-0.16	3538		
					3559	-0.43	3599		
					3507	-0.12	3519		
3067				3240					
2882				2893					
1584		0.11	1579	1564		0.01	1567		
1019		0.64	1002	1179		0.97	1082		
876		0.44	863	1039		0.58	978		
				901		0.34	872		
				759		0.47	713		
677		0.16	672	654		0.24	630		
636		0.18	632						
	554	1.05	524						
485		1.51	447	523					
454		1.48	413						
	398	1.04	369			0.63	458		
	263	0.49	249						
	219	0.18	213						
	147	0.11	144		159				
	118	0.00	117						
	81	0.00	82						
									157

† Intercept of least-squares line.

which corresponds to the distance between hydroxyl ions in adjacent unit cells along the c direction (O1–O2 in figures 1 and 2). There are short hydroxyl–water O–O distances, but formation of hydrogen bonds along them would not explain the strong coupling between the hydroxyls. If hydrogen-bonded chains were to form along c , no change in the size or symmetry of the unit cell would be required. The results, however, indicate that cell doubling occurs with the probable retention of a C_{2h} factor group as the IR and Raman components of hydroxyl stretch both split, but remain non-coincident. One possibility is that a small movement of the hydroxyl hydrogens (H1 and H2 in figure 1) to positions alternately above and below the mirror plane in which the ions lie, could occur along with a symmetric increase in the water–hydroxyl H-bond lengths, thereby forming zig-zag chains along c . This would yield a $I2/c$ structure with $z = 8$. There are however, other possibilities, such as those involving small changes in the position or orientation of the water molecules, and diffraction data are therefore required in order to determine the phase II structure.

Acknowledgments

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