

# CsOH and its Lighter Homologues – a Comparison

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 80<sup>th</sup> birthday*

Cesium hydroxide, CsOH, was for the first time characterised on the basis of single-crystal data. The structure is isotypic to the one of the room-temperature modification of NaOH and can be derived from the NaCl structure type thus allowing the comparison of all alkali metal hydroxide structures. Raman spectroscopic investigations show the hydroxide anion to behave almost as a free ion as in the gas phase. The X-ray investigations indicate possible H atom positions.

*Key words:* Alkali Metals, Cesium, Hydroxides, Crystal Structure, Vibration Spectroscopy

## Introduction

Among the most important chemical compounds for laboratory, industrial and household application count the alkali metal hydroxides. Their applications range from the production of paints and varnishes, household cleaners, glasses, aluminium and paper to mercerisation of cotton and food production. However, the structural elucidation of these simple compounds remained elusive for a long time. The highly hygroscopic and CO<sub>2</sub>-absorbant substances require sophisticated preparation methods. If not handled under strict exclusion of atmosphere, the hydroxides form numerous hydrates (see Table 1) or carbonates. Moreover, the hydroxides tend to crystallise poorly from solution or melts and form numerous modifications between room temperature and the respective melting points. Most of the for-

mer crystal structure descriptions therefore were based on powder data, and structural details remained elusive.

Several ways for the preparation of CsOH have been published [29–36], all of them requiring high preparative skills and elaborated equipment. During our investigations on suboxometallates of the heavy alkali metals [40–43] we found a new and simple method for the preparation of single-crystalline samples of CsOH. This method does not yield large amounts of the phase-pure substance but is suitable for the growth of large single crystals with high quality. It may be adapted for the lighter alkali metals and also for the preparation of deuterated samples.

The first crystal structure description of CsOH [36] attracted attention because of the especially weakly coordinated OH<sup>−</sup> anion. Compared to the vibrational fre-

Table 1. Alkali metal hydroxides and their hydrates.

Li	Na	K	Rb	Cs
LiOH [1–3]	NaOH [9–14]	KOH [9, 13]	RbOH [9, 13]	CsOH [29–36]
LiOH·H <sub>2</sub> O [4–8]	NaOH·H <sub>2</sub> O [15–17]	KOH·H <sub>2</sub> O [25, 26] KOH·2H <sub>2</sub> O [27]	RbOH·H <sub>2</sub> O [26] RbOH·2H <sub>2</sub> O [28]	CsOH·H <sub>2</sub> O [37, 38] CsOH·2H <sub>2</sub> O [39] CsOH·3H <sub>2</sub> O [39]
	NaOH·3.5H <sub>2</sub> O [17, 18] NaOH·4H <sub>2</sub> O [17, 19–22] NaOH·7H <sub>2</sub> O [18, 23, 24]	KOH·4H <sub>2</sub> O [27]		

Table 2. O–H stretching mode frequencies in alkali metal hydroxides ( $\text{cm}^{-1}$ ).

	Infrarot	Raman	Lit.
LiOH	3678	3664	[44–48]
NaOH	3637	3633	[49]
KOH	3600		[50–52]
CsOH		3589	this work
		3586	[53]
Gas phase		3556	[54–57]

quency of the hydroxide anion in the gas phase ( $3555.6 \text{ cm}^{-1}$  [54]),  $\nu_{\text{OH}}$  can be shifted either to higher or lower frequencies in solid hydroxides, depending on the nature and strength of  $M\text{--O}$  interactions. Covalent contributions to the  $M\text{--O}$  bond as *e.g.* in transition metal hydroxides and also  $\text{OH}^- \cdots X$  hydrogen bonding account for a decrease of  $\nu_{\text{OH}}$ . An increase of  $\nu_{\text{OH}}$  correlates with a decreasing  $M\text{--O}$  distance in the predominantly ionic alkali hydroxides [58]. Occurrence of additional hydrogen bonding between hydroxide anions and hydrate water molecules render the estimation of trends for the shift of  $\nu_{\text{OH}}$  very difficult.

## Results and Discussion

CsOH crystallises isotypically to the room-temperature modification of NaOH in the CrB (or as well anti-TII) structure type [59–62]. Details on data collection, crystallographic data, structure solution and refinement are given in Table 3. Standardised atomic coordinates [63] and isotropic displacement parameters are compiled in Table 4, the anisotropic displacement parameters and selected interatomic distances and angles can be found in Tables 5 and 6, respectively.

All cesium atoms occupy one single crystallographic position with Wyckoff-No. 4c and site symmetry  $m2m$ . Also the oxygen atoms occupy a 4c position. The Cs atoms are coordinated by O atoms in a square pyramid with Cs–O distances ranging from 296.5(15) to 315.2(3) pm. The Cs atom is shifted slightly from the centre of the square base towards the barycentre of the pyramid. The coordination sphere of Cs is completed by two O atoms with longer distances of 374(2) pm (see Fig. 1 and Table 6).

Table 3. Crystallographic data and selected details on the data collection, structure solution and refinement of CsOH.

Crystal system	orthorhombic
Space group	$Cmcm$ , (no. 63)
Lattice parameters, Å	<i>a</i> 4.3414(15) <i>b</i> 11.959(6) <i>c</i> 4.5036(14)
Volume, Å <sup>3</sup>	233.82(16)
Z	4
Calculated density, $\text{g cm}^{-3}$	4.23
Diffractometer	Stoe IPDS-I, $\text{MoK}\alpha$ radiation graphite-monochromatized
Data collection temperature, K	295
Absorption coefficient, $\text{mm}^{-1}$	15.4
Data range $2\theta$ , deg	5.00–27.50
Index range	$-5 \leq h \leq 5$ , $-15 \leq k \leq 15$ , $-5 \leq l \leq 5$
No. of observed reflections	1888
No. of independent reflections	164
No. of independent reflections with $[I > 2 \sigma(I)]$	150
$F(000)$ , <i>e</i>	252
Corrections	Absorption (numerical) [66, 67]
Structure solution	direct methods [68]
Structure refinement	least squares on $F^2$ [68, 69]
No. of l. s. parameters	9
Goof on $F^2$	1.208
$R1/wR2$ (for reflections with $I > 2 \sigma(I)$ )	0.0385 / 0.0850
$R1/wR2$ (all data)	0.0411 / 0.0859
Residual electron density (max. / min.), $e \text{ Å}^{-3}$	1.82 / $-1.12$
ICSD depository number	CSD-426540

Table 4. Standardised fractional atomic coordinates [63] and equivalent isotropic displacement parameters for CsOH. All atoms occupy crystallographic sites with Wyckoff-No.  $4c$  and point symmetry  $m2m$ . Standard deviations in units of the last digit are given in parentheses.

Atom	$x$	$y$	$z$	$U_{\text{eq}} (\text{\AA}^2)$
Cs1	0	0.35977(10)	$\frac{1}{4}$	0.0526(5)
O1	0	0.1118(13)	$\frac{1}{4}$	0.068(4)

Table 5. Anisotropic displacement parameters  $U_{ij}$  for CsOH ( $\text{\AA}^2$ ). Standard deviations in units of the last digit are given in parentheses.  $U_{12} = U_{13} = U_{23} = 0$  for all atoms.

Atom	$U_{11}$	$U_{22}$	$U_{33}$
Cs1	0.0445(6)	0.0650(8)	0.0482(8)
O1	0.058(9)	0.086(10)	0.059(9)

Table 6. Selected interatomic distances ( $\text{\AA}$ ) and angles (deg) for CsOH. Standard deviations in units of the last digit are given in parentheses. Only interatomic distances below 4.5 were taken into account.

Atoms	Distance	Atoms	Angle
Cs1–O1	2.965(15)	Cs1–O1–Cs1	83.8(3)
	3.1461(18)		87.25(6)
	3.714(12)		91.41(7)
Cs1–Cs1	4.040(25)		167.6(6)
	4.0836(19)	O1–Cs1–O1	60.6(3)
	4.3414(15)		71.5(3)
O1–O1	3.50(2)		87.25(6)
	4.341(2)		91.41(7)
			96.2(3)
			108.4(2)
			144.2(1)
			167.6(6)

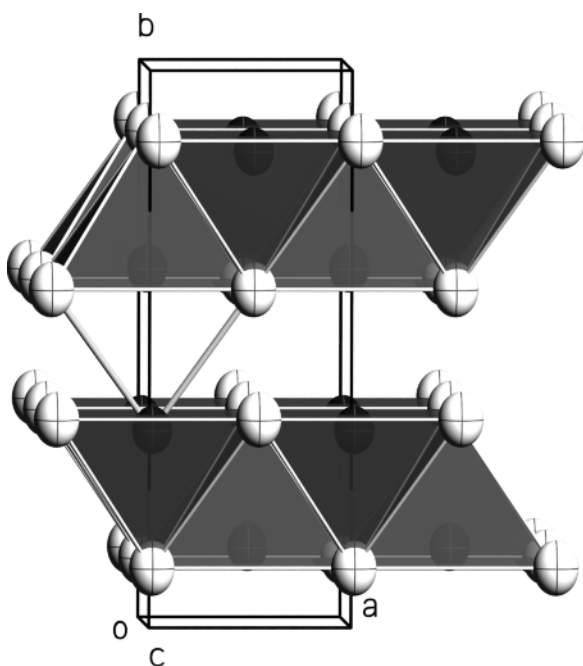


Fig. 1. The crystal structure of CsOH. All displacement ellipsoids are drawn on a probability level of 90%. Dark ellipsoids: Cs atoms, bright ellipsoids: O atoms. The additional contacts to O atoms in the neighbouring layer were drawn for the Cs atom in the lower left as light grey bonds.

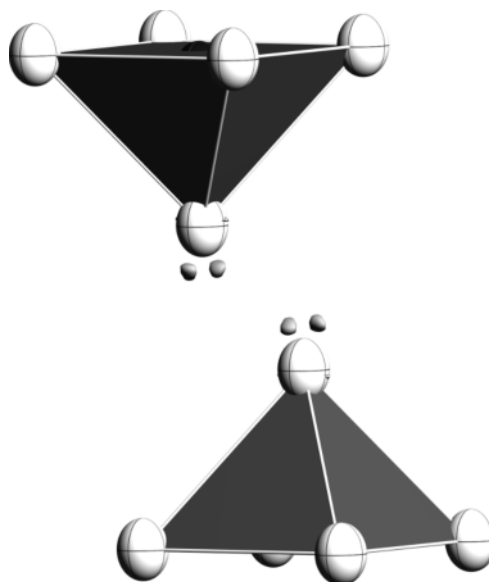


Fig. 2. The two maxima in the difference Fourier electron density map correspond to the H atom positions. The Fourier map was included in the structure drawing at a height of  $0.3 e \text{\AA}^{-3}$  [70].

The square pyramids  $[\text{Cs}_5\text{O}]$  are linked to sheets perpendicular to the crystallographic  $b$  axis *via* common edges. The additional contacts of Cs and O atoms belonging to adjacent sheets renders the CsOH structure to a 3D arrangement with no pronounced layer

compound character, in contrast to  $\text{Cs}_2\text{O}$  (anti- $\text{CdCl}_2$  structure) [64].

From the single-crystal data, no H atoms could be refined. However, a close analysis of the electron density in the difference Fourier map reveals two sharp

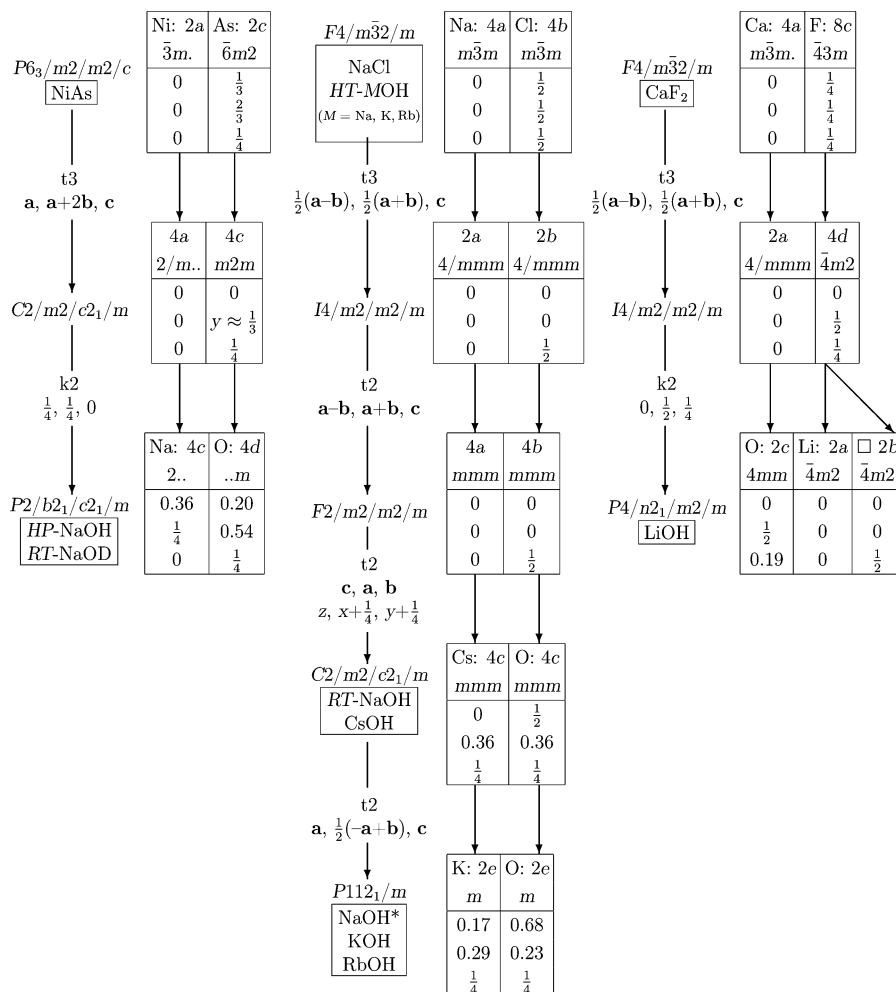


Fig. 3. Bärnighausen tree explaining the symmetric relations between the alkali metal hydroxides and their respective aristotypes. \*NaOH in space group  $P2_1/m$  is stable between 513 and 566 K.

maxima with about 0.5 electrons each and distances of 0.96 Å to the neighbouring O atom. These maxima can be assigned to the H atom positions and are in good agreement with the positions of D atoms obtained by neutron diffraction on CsOH samples [65], see Fig. 2.

The crystal structures of the anhydrous alkali metal hydroxides can be derived from simple structure types when all H atom positions are neglected (see Figs. 3 and 4).

LiOH crystallises in an anti-PbO structure with square nets of Li<sup>+</sup> cations capped alternately above and below the net plane by OH<sup>-</sup> anions (tetragonal, space group  $P4/nmm$ ) [1–3]. The structure can be derived from the CaF<sub>2</sub> structure type by remov-

ing one layer of F atoms. A structure with NaCl-type arrangement (cubic, space group  $Fm\bar{3}m$ ) is common to the high-temperature modifications of NaOH [12], KOH and RbOH [23]. At room temperature, NaOH and CsOH crystallise in an orthorhombic structure [23] (space group  $Cmcm$ ) which can be derived from the NaCl structure type by cutting out blocks and shifting them with respect to each other about  $a_{\text{NaCl}}/4$ . Shifting about  $a_{\text{NaCl}}/2$  leads to a monoclinic structure type (space group  $P2_1/m$ ) adopted by NaOH between 513 and 566 K and by KOH and RbOH at room temperature [26, 27]. A fourth structure (space group  $Pbcm$ ) can be derived from the NiAs structure type by slight distortions of all coordination polyhedra. It

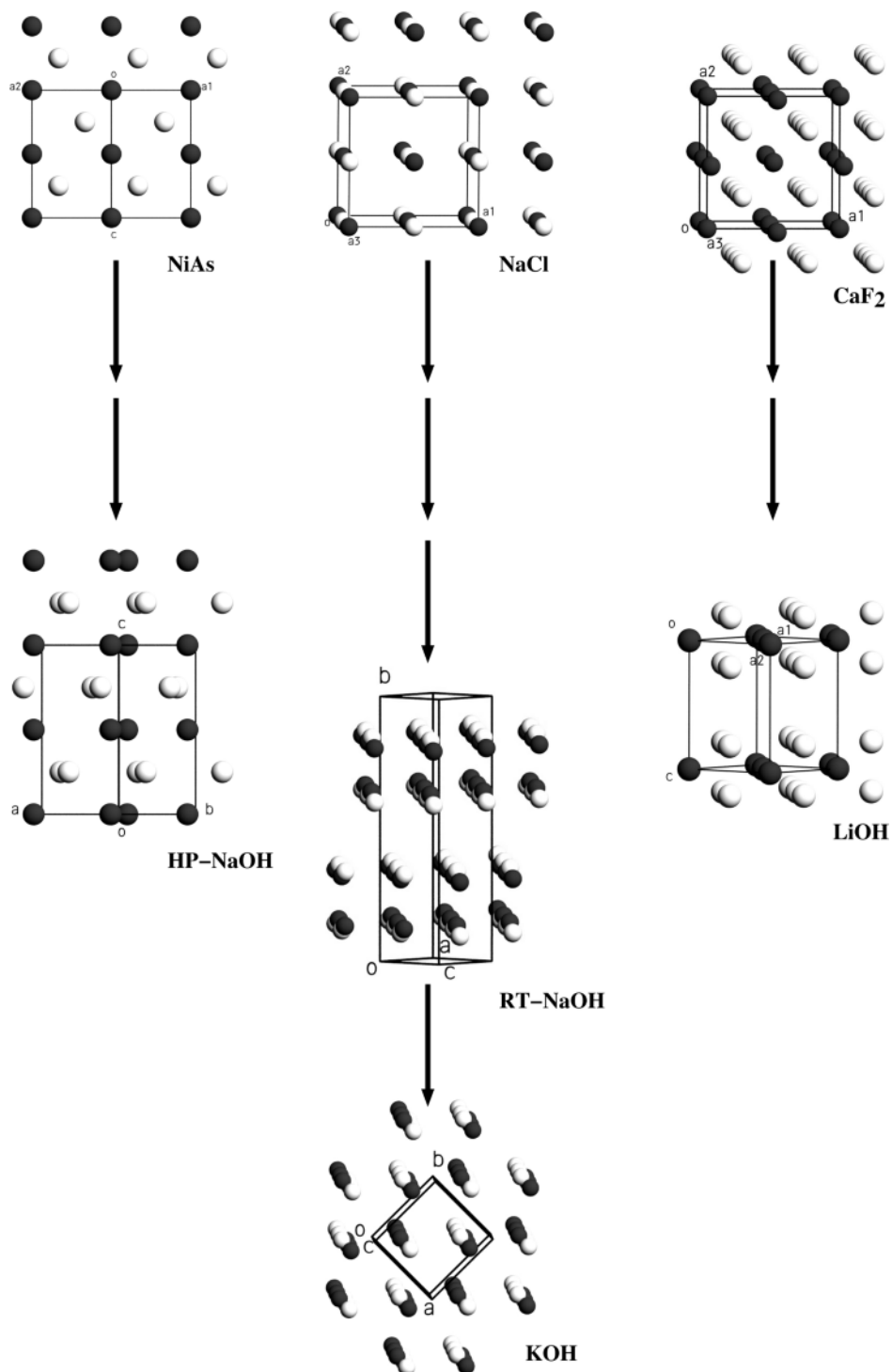


Fig. 4. Structural relations between alkali metal hydroxides and their aristotypes. The respective unit cells of the structures from Fig. 3 are drawn in projections which allow a direct comparison.

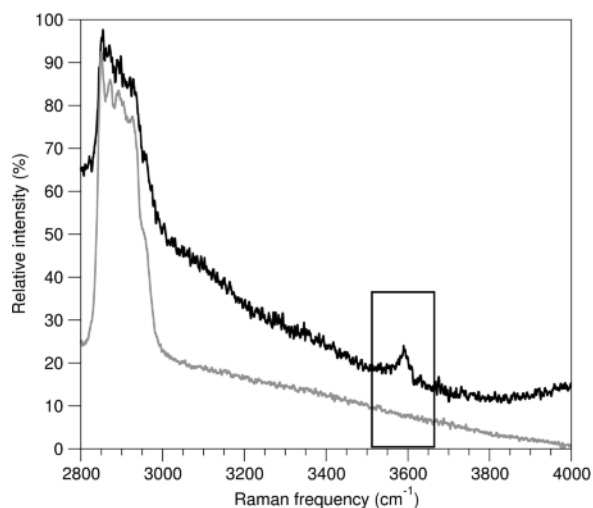


Fig. 5. Raman spectrum of a CsOH single crystal (black) and of a glass capillary filled with dry paraffin oil (gray). The signal in the box belongs to the characteristic O–H stretching mode of CsOH.

is adopted by a high-pressure modification of NaOH [71] and NaOD at ambient pressure [72]. This can be rationalised in analogy to the pressure-homologue rule [73], however, H is not substituted by its higher homologue but by its higher isotope.

#### Raman spectroscopy

The Raman spectrum of CsOH was recorded on the very same crystal used for the single-crystal X-ray analysis. It was sealed in a glass capillary filled with dry paraffin oil. The resulting spectrum thus contains contributions from C–H stretching and bending modes in the range of 1000 and 1500 and around 3000  $\text{cm}^{-1}$  in addition to the characteristic O–H stretching mode of CsOH at 3589  $\text{cm}^{-1}$  (see Fig. 5). It is very close to the one reported for powder samples of CsOH [53] and also to the one reported for the  $\text{OH}^-$  ion in the gas phase [54], see Table 2.

The crystal structures of the alkali metal hydroxides are a textbook example for the formal derivation of low-symmetric hettotype structures from simple and high-symmetric aristotype structures. The symmetry reduction can be explained by the chemical reason of distorting the respective structures by introducing a non-spherical hydroxide anion and thus distorting the local Coulomb potential. At high temperatures, the

$\text{OH}^-$  anion begins to rotate as a quasi-free particle, and the distortion is suppressed.

According to vibration-spectroscopical investigations, the  $\text{OH}^-$  anion in CsOH shows a behaviour only influenced by the M–O contacts, and the O–H stretching mode occurs at a frequency very close to the one of hydroxide anions in the gas phase, following the decrease of hardness of the alkali metal cations Li–Cs.

## Experimental Section

### Preparation and crystal structure investigation

Single crystals of CsOH were obtained by covering small portions of Cs metal in a petri dish inside an argon-filled glovebox with thoroughly dried paraffin oil and subsequently exposing the petri dish to air. After three days, CsOH single crystals had formed on the surface of the excess Cs metal by slow diffusion of air through the paraffin oil barrier. When all Cs metal is consumed, hydrates and finally the carbonate are formed. CsOH crystallises in brittle, transparent, irregularly shaped blocks and is very hygroscopic.

Single crystals suitable for X-ray investigations were selected under a binocular with polarisation filter and sealed in paraffin-filled glass capillaries with an inner diameter of 0.2 mm. They were centred on the one-circle goniometer of a diffractometer system IPDS1 (Stoe & Cie., Darmstadt, Germany) equipped with an imaging plate detector and graphite-monochromatised  $\text{MoK}\alpha$  radiation. The data of the accessible part of one Ewald sphere were collected and subsequently corrected for Lorentz, polarisation and absorption effects [66, 67]. The orthorhombic metric, the extinction conditions ( $hkl$ :  $h + k = 2n$  and  $h0l$ :  $l = 2n$ ) and the statistics on  $E^2 - 1$  indicated space group  $Cmcm$ . Structure solution [68] revealed all Cs and O atoms which were subsequently refined applying anisotropic displacement parameters [68]. Further details on the structure investigation may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)6247-808-666, e-mail: [crysddata@fiz-karlsruhe.de](mailto:crysddata@fiz-karlsruhe.de)), on quoting the deposition number CSD-426540.

### Raman spectroscopy

A He-Ne laser with a 1 mm focus in a confocal Raman microscope (LabRSM HG UV/Vis, Horiba Jobin Ivon GmbH, München, combined with an Olympus BX 41 microscope) equipped with a CCD detector was focussed on the capillary filled with paraffin oil and the CsOH single crystal. For the identification of the paraffin oil absorption bands, an identical spectrum was recorded at a position of the capillary where no CsOH crystal was in the focus.

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