

## Supplementary Material

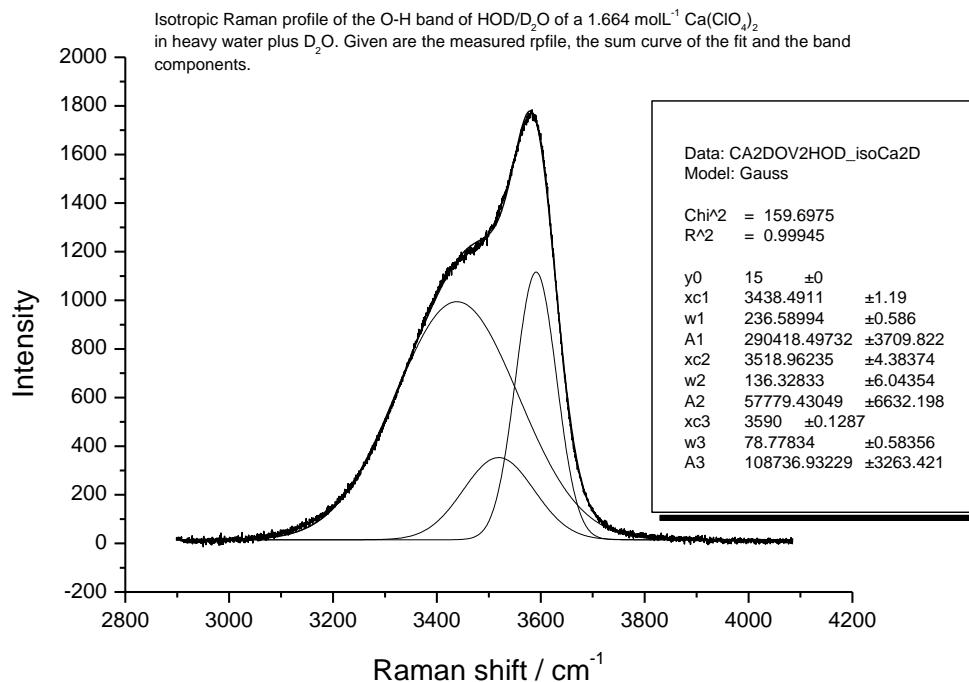


Figure S1.

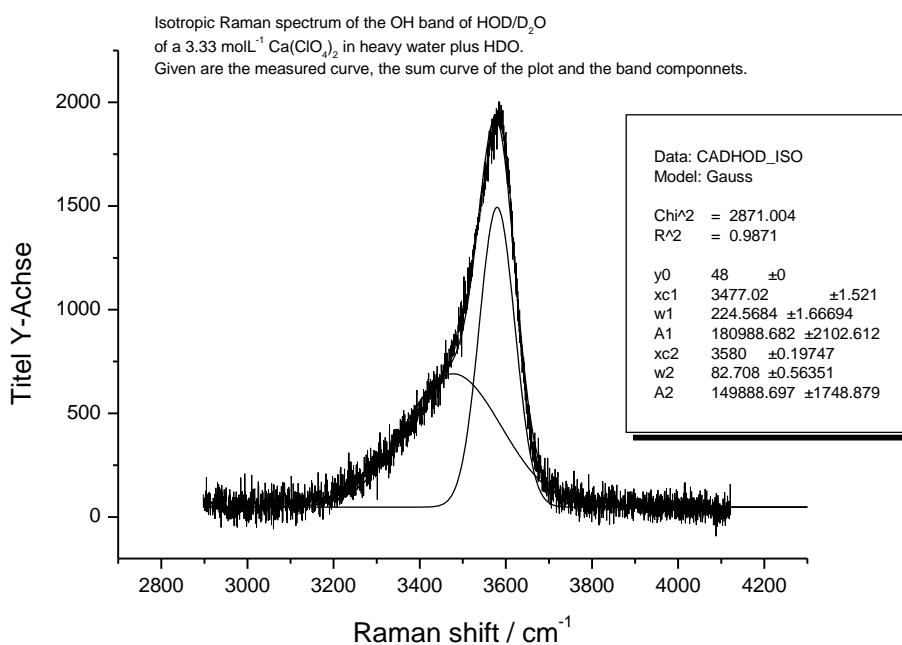
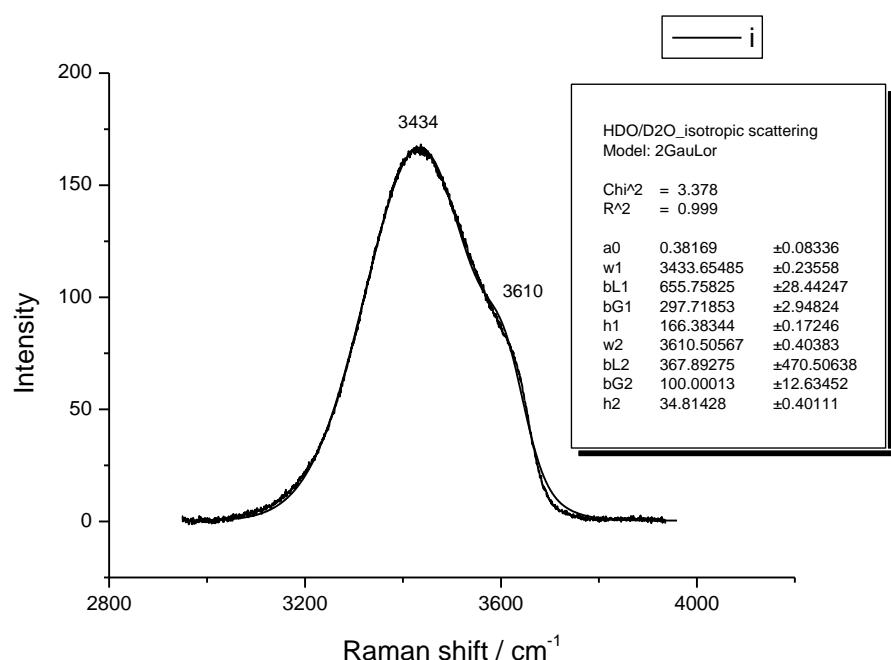
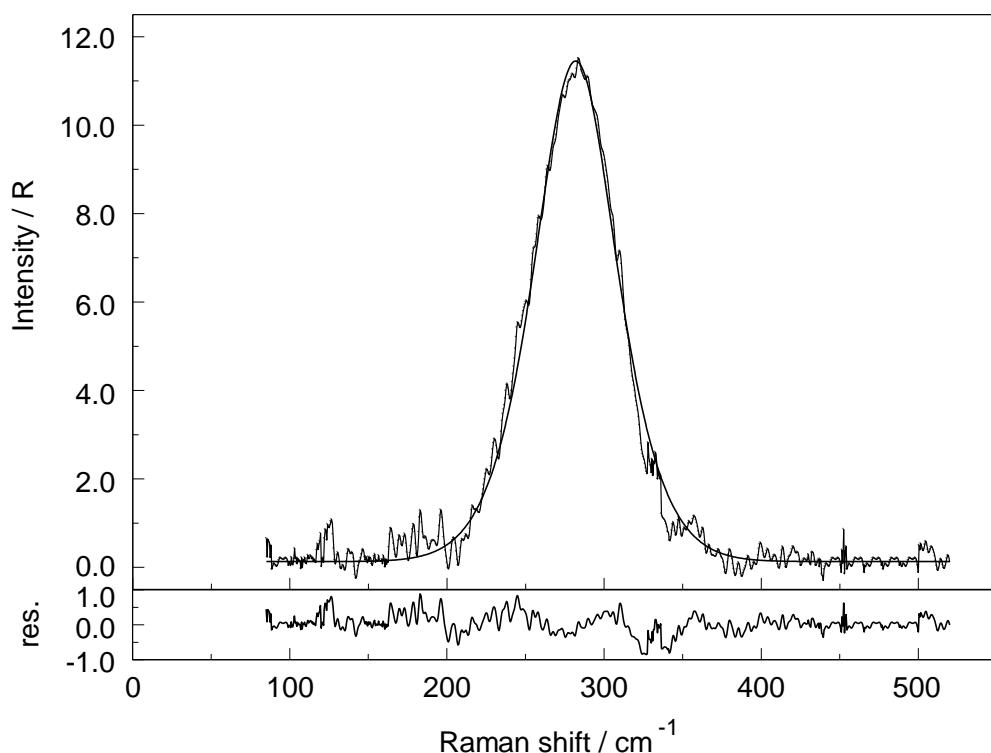


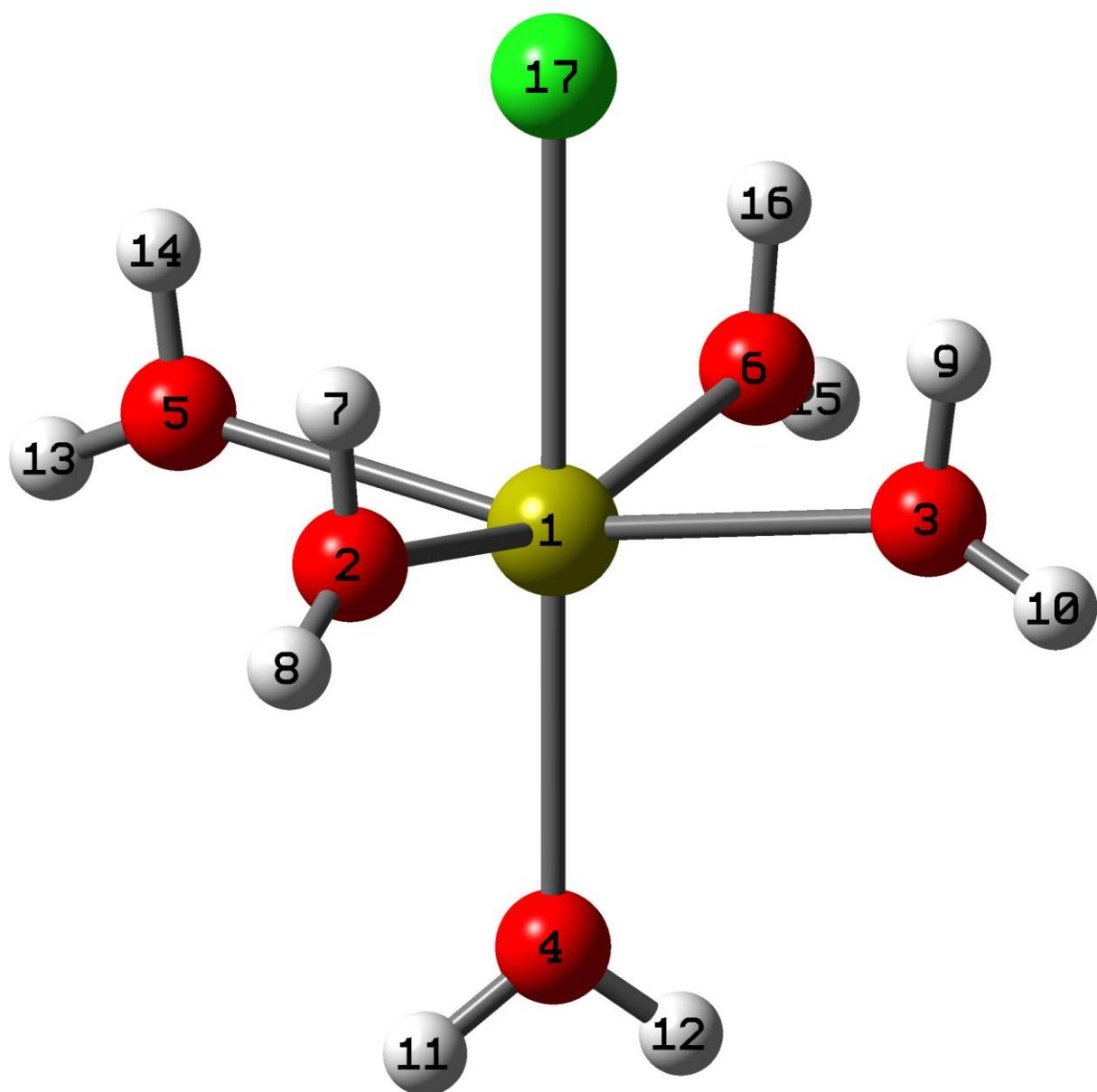
Figure S2.



**Fig. S3.** Band fit of the O-H band of HOD/D<sub>2</sub>O (~5 % HDO).



**Figure S4.** The baseline corrected, isotropic Raman mode of the symmetric stretch of Ca-O,  $\nu_1$ Ca-O of an aqueous 2.667 mol·L<sup>-1</sup> Ca(ClO<sub>4</sub>)<sub>2</sub> solution. The lower panel presents the residual curve of the difference between the measured and the fitted spectrum of  $\nu_1$ Ca-O.



**Figure S4.** Fully optimized structure of the contact ion pair,  $[\text{Ca}(\text{OH}_2)_5\text{Cl}]^+$ .

**Table S1**

DFT frequencies at the B3LYP/ 6-311+G(d,p) level of theory for the hexahydrate of  $\text{Ca}^{2+}$ ,  $\text{Ca}(\text{OH}_2)_6^{2+}$  and  $\text{Ca}(\text{OD}_2)_6^{2+}$  with additional solvation shell (PCM model)  
 symmetry  $T_h$

mode ( $T_h$ )			skeletal $\text{CaO}_6$ modes ( $O_h$ )	$\text{Ca}(\text{OH}_2)_6^{2+}$		$\text{Ca}(\text{OD}_2)_6^{2+}$		
				frequ. ( $\text{cm}^{-1}$ )	assign- ment	frequ. ( $\text{cm}^{-1}$ )	assign- ment	$r = \frac{v_{\text{Ca}(\text{OH}_2)_6^{2+}}}{v_{\text{Ca}(\text{OD}_2)_6^{2+}}}$
1	$f_u$	i.r.	$v_6(f_{2u})$ -	39.9	$\delta \text{CaO}_6$	36.4	$\delta \text{CaO}_6$	1.100
2	$f_g$	Ra	$v_5(f_{2g})$ Ra	67.7	$\delta \text{CaO}_6$	61.7	$\delta \text{CaO}_6$	1.100
3	$f_u$	i.r.	$v_3(f_{1u})$ i.r.	77.9	$\delta \text{CaO}_6$	71.9	$\delta \text{CaO}_6$	1.083
4	$e_g$			83.0	$\tau \text{HOH}$	58.7	$\tau \text{DOD}$	1.414
5	$f_g$	Ra		137.8	$\tau \text{HOH}$	98.3	$\tau \text{DOD}$	1.402
6	$a_g$	-		207.1	$\tau \text{HOH}$	146.5	$\tau \text{DOD}$	1.414
7	$e_g$	Ra	$v_2(e_g)$ Ra	<b>262.3</b>	$v_s \text{CaO}_6$	<b>248.6</b>	$v_s \text{CaO}_6$	<b>1.055</b>
8	$f_g$	Ra		270.8	$\omega \text{H-O-H}$	208.7	$\omega \text{DOD}$	1.298
9	$f_u$	i.r.		271.2	$\omega \text{H-O-H}$	210.9	$\omega \text{DOD}$	1.286
10	$a_g$	Ra	$v_1(a_{1g})$ Ra	<b>285.8</b>	$v_s \text{CaO}_6$	<b>271.2</b>	$v_s \text{CaO}_6$	<b>1.054</b>
11	$f_u$	i.r.	$v_4(f_{1u})$ i.r.	341.7	$v_{as} \text{CaO}_6$	306.1	$v_{as} \text{CaO}_6$	1.120
12	$f_g$	Ra		424.9	$\rho \text{HOH}$	319.3	$\rho \text{DOD}$	1.331
13	$f_u$	i.r.		433.9	$\rho \text{HOH}$	353.7	$\rho \text{DOD}$	1.227
14	$f_u$	i.r.		1623.5	$\delta \text{HOH}$	1190.0	$\delta \text{DOD}$	1.364
15	$e_g$	Ra		1623.5	$\delta \text{HOH}$	1189.8	$\delta \text{DOD}$	1.364
16	$a_g$	Ra		1626.2	$\delta \text{HOH}$	1191.2	$\delta \text{DOD}$	1.365
17	$e_g$	Ra		3730.2	$v_s \text{OH}$	2687.0	$v_s \text{OD}$	1.388
18	$f_u$	i.r.		3731.2	$v_s \text{OH}$	2687.5	$v_s \text{OD}$	1.388
19	$a_g$	Ra		3735.9	$v_s \text{OH}$	2689.7	$v_s \text{OD}$	1.388
20	$f_g$	Ra		3800.9	$v_{as} \text{OH}$	2785.0	$v_{as} \text{OD}$	1.365
21	$f_u$	i.r.		3800.9	$v_{as} \text{OH}$	2785.1	$v_{as} \text{OD}$	1.365

isotopic frequency shift:

An important indicator of the frequency mode and its symmetry is given by comparison of the vibrational frequencies in deuterated and undeuterated solutions.

For the cluster  $[\text{Ca}(\text{OH}_2)_6]^{2+}$  and  $[\text{Ca}(\text{OD}_2)_6]^{2+}$  this ratio  $r$  is given in the last row of Table S1

For the modes identified as skeletal modes, the water molecules do not vibrate.

The lowest values with about 1.055 are obtained for the symmetric stretching vibrations of the cluster. For these modes the water molecules translate along the  $\text{Ca} - \text{O}$  bond stretching, the ratio  $r$  is determined by the mass ratio D/H and can be obtained using equ. (7). The other skeletal modes involve in addition rotations of the water molecules and the ratio  $r$  also depends on the different moments of inertia of the undeuterated/deuterated cluster ions. Whereas for the skeletal deformation modes (modes 1-3) the water molecules rotate around axes through the  $\text{Ca}^{2+}$  ion, the largest ratios  $r$  are obtained for twist movements of the water molecules around the fixed skeletal  $\text{Ca} - \text{O}$  axes (modes 4-6).

**Table S2**

DFT frequencies at the B3LYP/ 6-311+G(d,p) level of theory for the octadecahydrate  $\text{Ca}(\text{OH}_2)_{18}]^{2+}$  or better written as  $[\text{Ca}(\text{OH}_2)_6(\text{OH}_2)_{12}]^{2+}$  with symmetry T.

frequ. $\text{cm}^{-1}$	symm.		mode	frequ. $\text{cm}^{-1}$	symm.		mode
30.6	F	Ra	rot. $(\text{H}_2\text{O})_3$	562.7	A	Ra	$\tau, \rho$ HOH
34.2	A	Ra	rot. $(\text{H}_2\text{O})_3$	577.2	A	Ra	$\tau, \rho$ HOH
42.3	E	Ra	trans. $(\text{H}_2\text{O})_3$	600.6	F	i.r. Ra	$\omega, \rho$ HOH
53.5	F	i.r. Ra	trans. $(\text{H}_2\text{O})_3, \text{CaO}_6$	666.0	F	i.r. Ra	$\omega$ HOH
75.3	F	i.r. Ra	rot. $(\text{H}_2\text{O})_3, \text{CaO}_6$	682.5	E	Ra	$\omega, \tau$ HOH
84.0	F	i.r. Ra	rot. $(\text{H}_2\text{O})_3, \text{CaO}_6$	710.5	F	i.r. Ra	$\omega, \tau$ HOH
93.0	F	i.r. Ra	rot. $(\text{H}_2\text{O})_3 + \delta \text{CaO}_6$	756.4	F	i.r. Ra	$\rho$ HOH
123.1	E	Ra	rot. $(\text{H}_2\text{O})_3 + v_{\text{as}} \text{CaO}_6$	790.8	F	i.r. Ra	$\rho$ HOH
131.7	F	i.r. Ra	trans. $(\text{H}_2\text{O})_3 + \delta \text{CaO}_6$	866.3	F	i.r. Ra	$\omega$ HOH
139.8	A	Ra	trans. $(\text{H}_2\text{O})_3$	867.0	A	Ra	$\omega$ HOH
147.1	F	i.r. Ra	trans. $(\text{H}_2\text{O})_3 + \delta \text{CaO}_6$	1635.1	F	i.r. Ra	$\delta$ HOH
154.7	F	i.r. Ra	trans. $(\text{H}_2\text{O})_3 + \delta \text{CaO}_6$	1635.2	E	Ra	$\delta$ HOH
183.2	F	i.r. Ra	trans. $(\text{H}_2\text{O})_3 + \delta \text{CaO}_6$	1635.9	F	i.r. Ra	$\delta$ HOH
184.2	E	Ra	trans. $(\text{H}_2\text{O})_3$	1637.0	F	i.r. Ra	$\delta$ HOH
204.6	F	i.r. Ra	trans. $(\text{H}_2\text{O})_3$	1637.9	A	Ra	$\delta$ HOH
207.1	A	Ra	trans. $(\text{H}_2\text{O})_3$	1698.0	E	Ra	$\delta$ HOH
229.8	F	Ra	$\delta \text{CaO}_6 + \text{trans. } (\text{H}_2\text{O})_3$	1701.2	F	i.r. Ra	$\delta$ HOH
237.6	F	i.r. Ra	$\delta \text{CaO}_6 + \text{trans. } (\text{H}_2\text{O})_3$	1712.0	A	Ra	$\delta$ HOH
287.7	E	Ra	$v_{\text{as}} \text{CaO}_6$	3571.9	E	Ra	$v_s$ OH
305.3	A	Ra	$v_s \text{CaO}_6$	3578.9	F	i.r. Ra	$v_s$ OH
345.8	F	i.r. Ra	$\rho$ HOH	3594.1	A	i.r. Ra	$v_s$ OH
348.1	F	i.r. Ra	$v_{\text{as}} \text{CaO}_6 + \rho$ HOH	3595.0	F	i.r. Ra	$v_s$ OH
361.0	E	Ra	$\rho$ HOH	3607.9	F	i.r. Ra	$v_s$ OH
361.6	F	i.r. Ra	$v_{\text{as}} \text{CaO}_6 + \rho$ HOH	3615.3	A	i.r. Ra	$v_s$ OH
408.0	F	i.r. Ra	$\rho$ HOH	3641.7	F	i.r. Ra	$v_s$ OH + $v_{\text{as}}$ OH
437.6	A	i.r. Ra	$\omega$ HOH	3659.0	E	Ra	$v_s$ OH
447.4	F	i.r. Ra	$\rho$ HOH	3669.5	F	i.r. Ra	$v_s$ OH + $v_{\text{as}}$ OH
476.6	F	i.r. Ra	$\rho$ HOH	3675.1	F	i.r. Ra	$v_s$ OH + $v_{\text{as}}$ OH
483.2	E	Ra	$\rho$ HOH	3852.8	F	i.r. Ra	$v_{\text{as}}$ OH
522.0	F	i.r. Ra	$\tau$ HOH	3853.3	F	i.r. Ra	$v_{\text{as}}$ OH
525.5	F	i.r. Ra	$\tau$ HOH	3853.4	E	Ra	$v_{\text{as}}$ OH
526.9	E	Ra	$\tau$ HOH	3857.0	F	i.r. Ra	$v_{\text{as}}$ OH
540.6	F	i.r. Ra	$\tau, \rho$ HOH	3857.6	A	Ra	$v_{\text{as}}$ OH

**Table S3** DFT geometrical parameters from DFT calculations at the B3LYP/ 6-311+G(d,p) level for the octadecahydrate  $\text{Ca}(\text{OH}_2)_{18}]^{2+}$  or better written as  $[\text{Ca}(\text{OH}_2)_6(\text{OH}_2)_{12}]^{2+}$  with symmetry T.

structural parameter	$\text{Ca}(\text{OH}_2)_{18}^{2+}$
Ca – O (inner sphere) (Å)	2.383
O – H (inner sphere) (Å)	0.975
H-O-H (inner sphere) (°)	108.02
Ca – O (outer sphere) (Å)	4.475
O – H(A) (outer sphere) (Å)	0.965
O – H(B) (outer sphere) (Å)	0.975
H-O-H (outer sphere) (°)	106.94
H ... OH bond length (Å)	1.879

**Table S4**

DFT frequencies at the HF/ 6-311+G(d,p) level of theory for the cluster  $[\text{Ca}(\text{OH}_2)_5\text{Cl}]^+$ , symmetry  $\text{C}_{2v}$

vibration			freq. $\text{cm}^{-1}$	mode	vibration			freq. $\text{cm}^{-1}$	mode
1	B <sub>1</sub>	i.r. Ra	60.1	$\delta \text{OCaCl}$	24	A <sub>2</sub>	Ra	565.0	$\rho \text{HOH}$
2	B <sub>2</sub>	i.r. Ra	64.5	$\delta \text{OCaCl}$	25	B <sub>2</sub>	i.r. Ra	584.5	$\omega \text{HOH}$
3	B <sub>2</sub>	Ra	80.3	$\delta \text{OCaO}$	26	B <sub>1</sub>	i.r. Ra	585.1	$\omega \text{HOH}$
4	B <sub>2</sub>	i.r. Ra	93.4	$\delta \text{OCaO}$	27	B <sub>1</sub>	i.r. Ra	592.1	$\rho \text{HOH}$
5	B <sub>1</sub>	i.r.Ra	94.4	$\delta \text{OCaO}$	28	B <sub>2</sub>	i.r. Ra	595.5	$\rho \text{HOH}$
6	A <sub>1</sub>	i.r. Ra	104.8	$\delta \text{OCaO}$	29	A <sub>1</sub>	i.r. Ra	619.6	$\omega \text{HOH}$
7	B <sub>1</sub>	i.r.Ra	114.1	$\delta \text{OCaO}$	30	A <sub>1</sub>	i.r. Ra	635.6	$\rho \text{HOH}$
8	B <sub>2</sub>	i.r.Ra	116.3	$\delta \text{OCaO}$	31	A <sub>2</sub>	Ra	1783.9	$\delta \text{HOH}$
9	A <sub>1</sub>	i.r. Ra	118.9	$\delta \text{OCaO}$	32	B <sub>1</sub>	i.r. Ra	1786.0	$\delta \text{HOH}$
<b>10</b>	<b>A<sub>1</sub></b>	<b>i.r. Ra</b>	<b>209.3</b>	<b><math>\nu_s \text{OCaCl}</math></b>	33	B <sub>2</sub>	i.r. Ra	1786.3	$\delta \text{HOH}$
11	A <sub>2</sub>	Ra	215.6	$\nu_s \text{OCaO}$	34	A <sub>1</sub>	i.r. Ra	1796.6	$\delta \text{HOH}$
<b>12</b>	<b>A<sub>1</sub></b>	<b>i.r.Ra</b>	<b>242.1</b>	<b><math>\nu_s \text{OCaCl}</math></b>	35	A <sub>1</sub>	i.r. Ra	1807.2	$\delta \text{HOH}$
13	B <sub>1</sub>	i.r. Ra	292.3	$\nu_{as} \text{OCaO}$	36	A <sub>2</sub>	Ra	3972.7	$\nu_s \text{OH}$
14	B <sub>2</sub>	i.r. Ra	292.8	$\nu_{as} \text{OCaO}$	37	B <sub>1</sub>	i.r. Ra	3974.7	$\nu_s \text{OH}$
<b>15</b>	<b>A<sub>1</sub></b>	<b>i.r.Ra</b>	<b>310.0</b>	<b><math>\nu_{as} \text{OCaCl}</math></b>	38	B <sub>2</sub>	i.r. Ra	3974.8	$\nu_s \text{OH}$
16	A <sub>2</sub>	Ra	339.5	$\tau \text{HOH}$	39	A <sub>1</sub>	i.r. Ra	3980.0	$\nu_s \text{OH}$
17	A <sub>2</sub>	Ra	366.6	$\tau \text{HOH}$	40	A <sub>1</sub>	i.r. Ra	4001.5	$\nu_s \text{OH}$
18	A <sub>1</sub>	i.r. Ra	391.4	$\tau \text{HOH}$	41	B <sub>2</sub>	i.r. Ra	4078.0	$\nu_{as} \text{OH}$
19	B <sub>1</sub>	i.r. Ra	394.1	$\tau \text{HOH}$	42	A <sub>2</sub>	Ra	4094.5	$\nu_{as} \text{OH}$
20	A <sub>1</sub>	i.r. Ra	421.3	$\tau \text{HOH}$	43	B <sub>2</sub>	i.r. Ra	4095.0	$\nu_{as} \text{OH}$
21	A <sub>2</sub>	Ra	511.4	$\omega \text{HOH}$	44	B <sub>1</sub>	i.r. Ra	4095.1	$\nu_{as} \text{OH}$
22	B <sub>1</sub>	i.r. Ra	531.6	$\omega \text{HOH}$	45	A <sub>1</sub>	i.r. Ra	4097.2	$\nu_{as} \text{OH}$
23	B <sub>2</sub>	i.r. Ra	541.6	$\rho \text{HOH}$					

**Table S5.** Structural parameters for the cluster from DFT calculations at the HF/ 6-311+G(d,p) level of theory for the cluster  $[\text{Ca}(\text{OH}_2)_5\text{Cl}]^+$ ; symmetry  $\text{C}_{2v}$ .

bond length (in Å)		angle	
		(deg)	
Ca – Cl	2.6789	O(2)- Ca - Cl	81.17
Ca – O(4)	2.4650	O(2)-Ca - O(5)	89.13
Ca – O(2,3,5,6)	2.4518	H(7)- O(2)- H(8)	107.40
O(3) –H(9)	0.9553	H(11)- O(4)- H(12)	106.09
O(3) –H(10)	0.9500	Ca - O(2) - H(7)	106.24
O(4) –H(11)	0.9526		