

Supplementary Material

Table S1. Geometrical parameters for the cluster $\text{CH}_3\text{CO}_2^- \cdot n\text{H}_2\text{O} \cdot m\text{H}_2\text{O}$; bond lengths a_{ij} (in Å), angles α_{ijk} and dihedral angle d_{4215} of the CH_3CO_2^- ion (see Fig. 1) derived from DFT calculations (B3LYP/ 6-311++G(3df,2pfd)).

parameter	CH_3CO_2^- <i>in vacuo</i>	CH_3CO_2^- $\cdot\text{H}_2\text{O}$	CH_3CO_2^- $\cdot 2\text{H}_2\text{O}$	CH_3CO_2^- $\cdot 4\text{H}_2\text{O}$	CH_3CO_2^- $\cdot 5\text{H}_2\text{O}$	CH_3CO_2^- $\cdot 5\text{H}_2\text{O} \cdot \text{H}_2\text{O}$
$a_{1,2}$	1.561	1.548	1.542	1.532	1.526	1.524
$a_{2,3}$	1.253	1.257	1.261	1.259	1.269	1.269
$a_{2,4}$	1.252 ₅	1.256	1.251	1.257	1.250	1.252
$a_{1,5}$	1.091	1.090	1.089	1.088	1.087	1.087
$a_{1,6}$	1.093	1.092	1.093	1.092	1.089	1.089
$a_{1,7}$	1.093	1.093	1.091	1.090	1.092	1.092
$\alpha_{3,2,4}$	128.84°	127.78°	127.71°	126.06°	125.03°	124.74°
$\alpha_{5,1,6}$	109.51°	109.90°	108.87°	108.96°	110.55°	110.64°
$\alpha_{5,1,7}$	109.51°	109.26°	110.29°	110.33°	108.88°	108.75°
$\alpha_{6,1,7}$	107.03°	107.13°	107.28°	107.31°	107.18°	107.29°
$d_{4,2,1,5}$	0°	0°	-13.07°	-12.66°	14.71°	17.31°
$a_{3,10}$	-	1.991	-	-	-	-
$a_{4,9}$	-	2.014	1.830	1.758	1.756	1.686
$a_{3,12}$	-	-	1.674	1.903	2.032	2.020
$a_{4,15}$	-	-	-	1.984	2.016	1.963
$a_{3,18}$	-	-	-	1.945	1.947	1.924
$a_{3,21}$	-	-	-	-	1.781	1.789

n.a. = not applicable

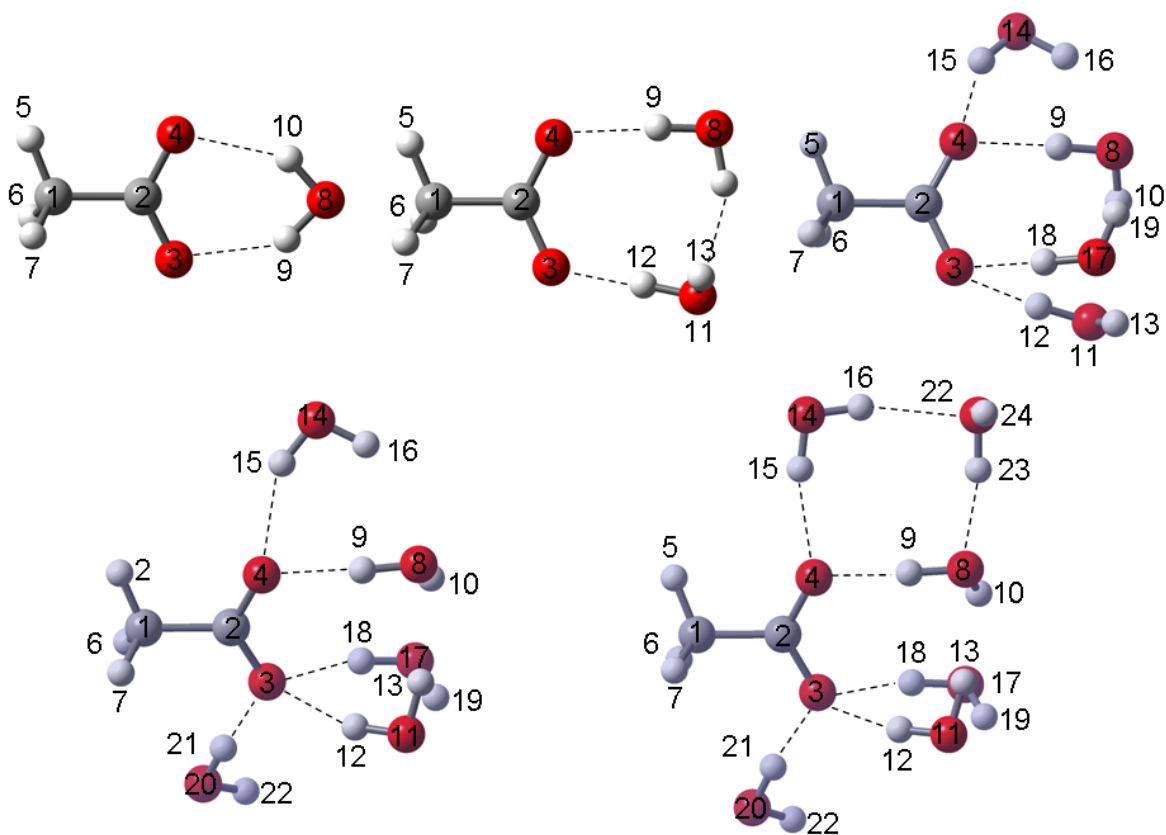


Figure S1. Five selected acetate-water clusters with different numbers of water molecules; $\text{CH}_3\text{CO}_2^- \cdot n\text{H}_2\text{O} \cdot m\text{H}_2\text{O}$ ($n = 1-5$, $m=1$).

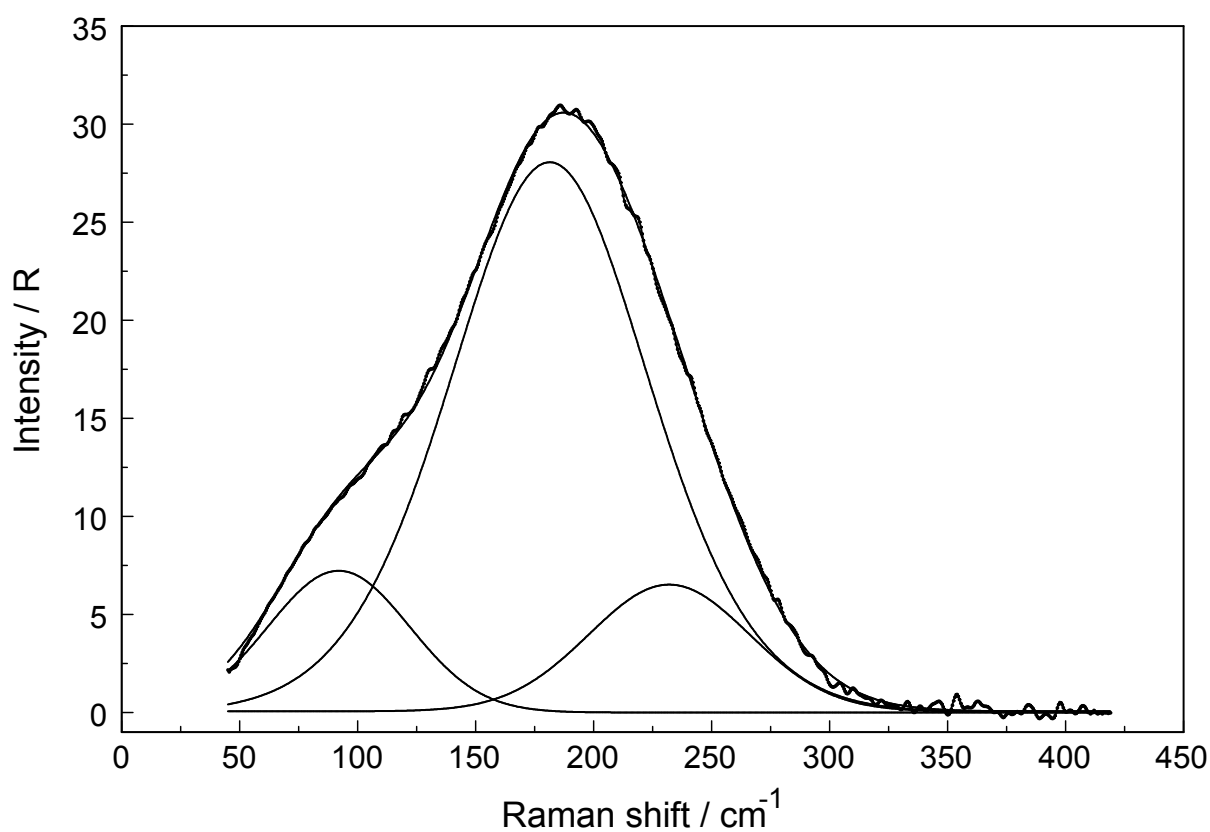


Figure S2. Band fit of the isotropic Raman profile of NaCH₃CO₂(D₂O) at 3.944 mol·L⁻¹. Given are also the band components at 90 cm⁻¹, the restricted bending mode at 181 cm⁻¹, the Na-O breathing mode of the Na⁺(D₂O) and at 233 cm⁻¹ the stretching mode of the restricted stretch, ν_s O-D···O, reflecting the D-bonds between oxygen atoms of the -CO₂⁻ group and D₂O.

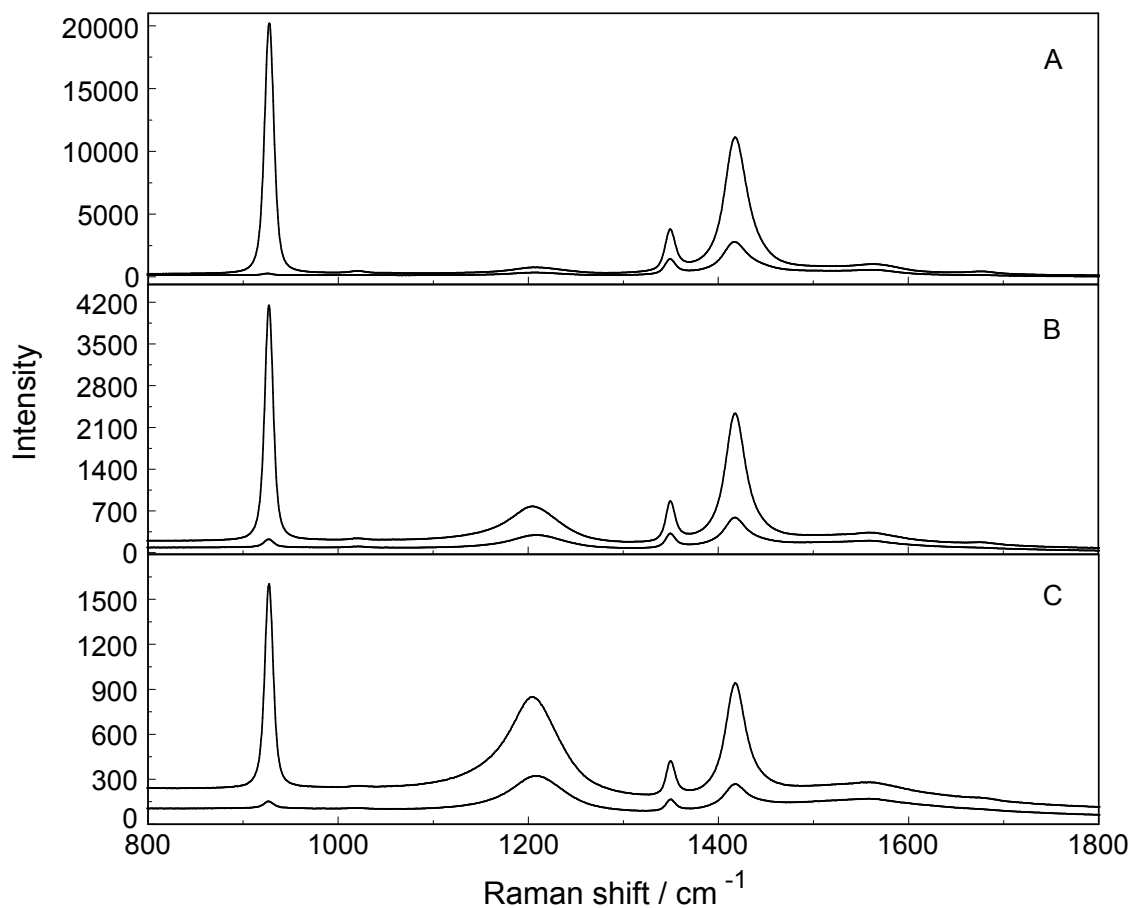


Figure S3. Raman spectroscopic concentration profile of $\text{NaCH}_3\text{CO}_2(\text{D}_2\text{O})$: A) $3.944 \text{ mol}\cdot\text{L}^{-1}$, B) $0.789 \text{ mol}\cdot\text{L}^{-1}$, C) $0.263 \text{ mol}\cdot\text{L}^{-1}$. Given are the polarized and depolarized spectra. The broad band at 1206 cm^{-1} is assigned to the deformation mode of heavy water. Note, that the symmetric stretching band, $\nu_s \text{CO}_2$ at 1414 cm^{-1} shows an intrinsically asymmetric profile due to overlap with two deformation modes of the CH_3 group at 1426 and 1440 cm^{-1} . In contrast to $\text{NaCD}_3\text{CO}_2(\text{H}_2\text{O}/\text{D}_2\text{O})$ however, the symmetric stretching band, $\nu_s \text{CO}_2$ at 1408 cm^{-1} shows a symmetric profile, because of the vibrational deuteration effect of the CD_3 group to much lower wavenumbers. See spectrum in Figure 7.

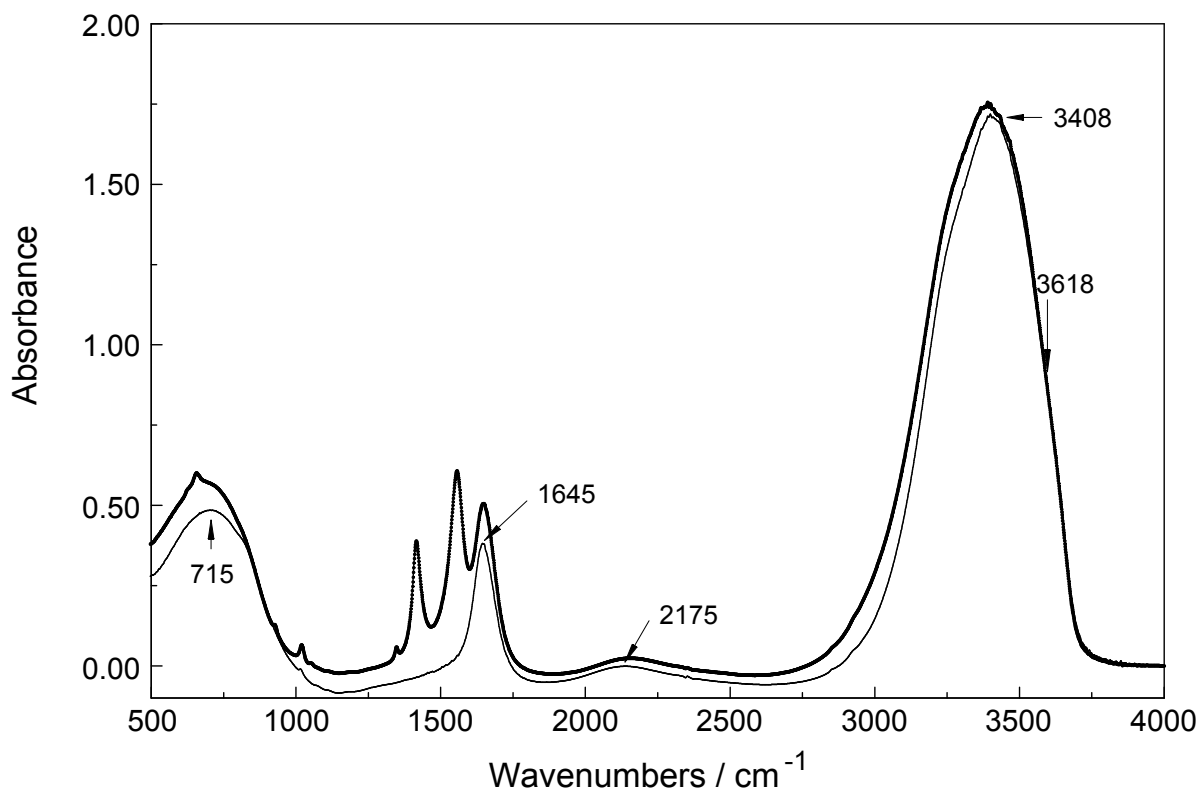


Figure S4. Infrared absorption spectra of neat water (lower spectrum) and of an aqueous 2.184 molL⁻¹ NaCH₃CO₂ solution ($R_w = 22.9$), (upper spectrum, presented as a thick, dark line). For the water spectrum the band positions are: broad band 715 cm⁻¹ assigned to librational band, ν_L of H₂O (in NaCH₃CO₂(aq) ν_L is shifted to 690 cm⁻¹); band at 1645 cm⁻¹ assigned to deformation mode, the broad band at 2170 cm⁻¹ is a combination band and the O-H stretching band profile peaking at 3408 cm⁻¹ plus a shoulder at 3616 cm⁻¹. It becomes obvious that the high frequency part of the water O-H band and from the NaCH₃CO₂ solution are quite similar while the peak position of the O-H band of NaCH₃CO₂(aq) is shifted to lower frequencies, the overall O-H band profile is broadened and the band peaks at 3395 cm⁻¹.

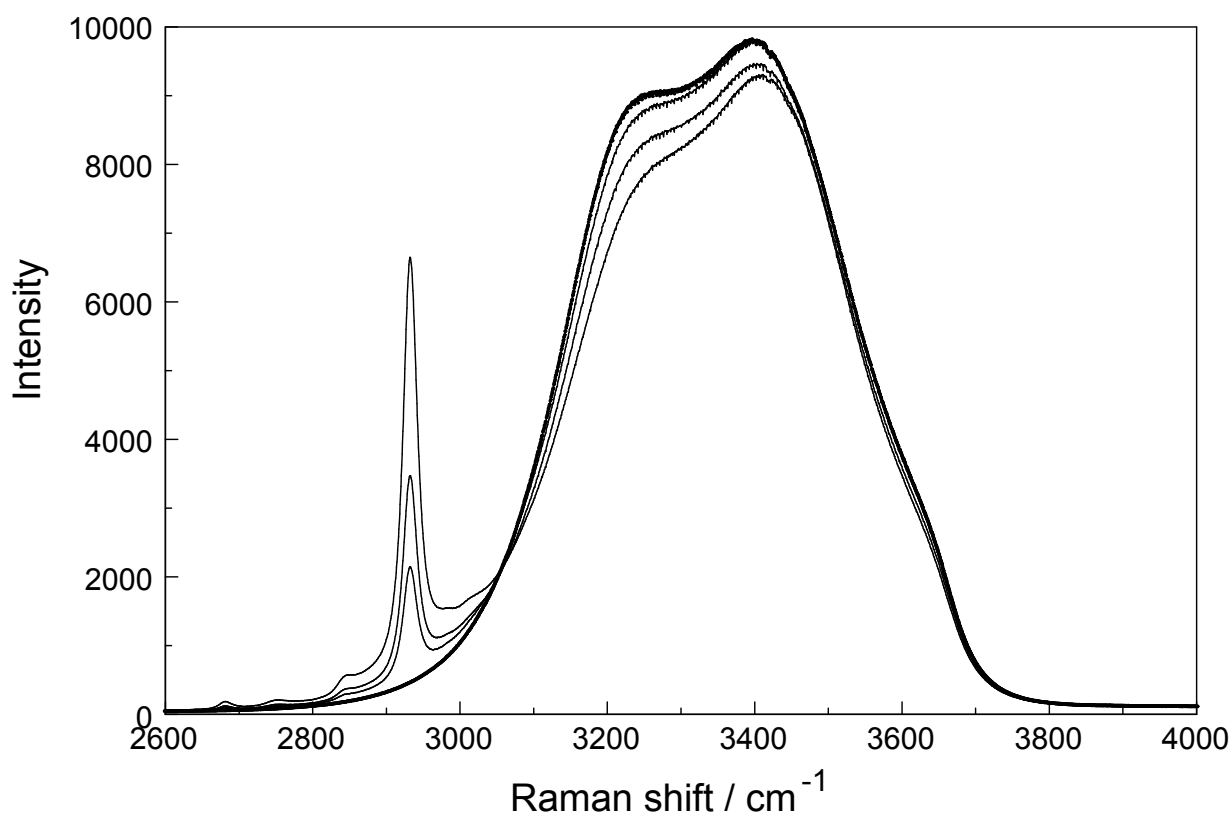


Figure S5. Polarized Raman profiles of three aqueous NaCH_3CO_2 solutions and water. Band profiles from bottom to top: neat H_2O , 0.604 molL^{-1} , 1.094 molL^{-1} and 2.208 molL^{-1} $\text{NaCH}_3\text{CO}_2(\text{aq})$. Note the C-H stretching bands at 2935 cm^{-1} of $\text{NaCH}_3\text{CO}_2^-(\text{aq})$, the broad O-H double band at 3210 and 3430 cm^{-1} as well as the broad shoulder at 3630 cm^{-1} due to the O-H stretching band profiles.

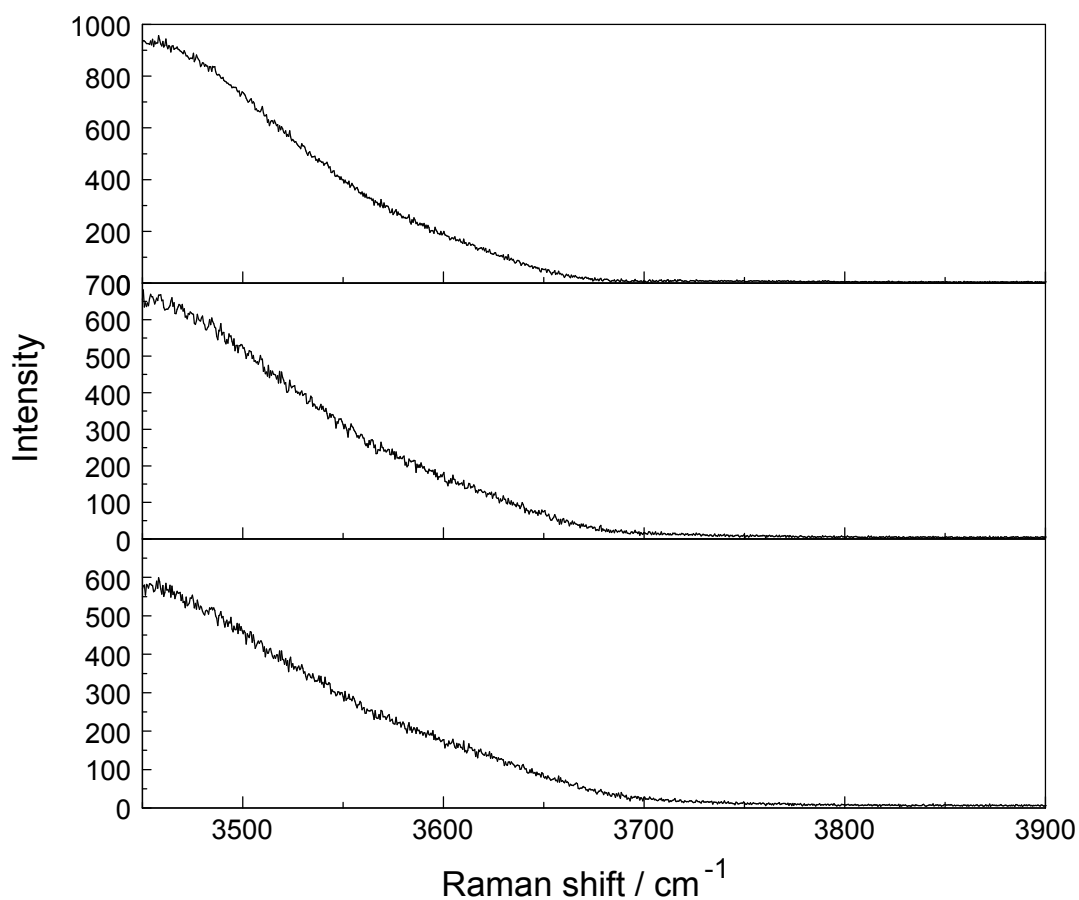


Figure S6. Raman difference spectra of polarized the O-H bands of $\text{NaCH}_3\text{CO}_2(\text{aq})$ from 0.604 to 2.208 molL^{-1} (see also Figure S4). The water band has been subtracted from each solute spectrum. Concentration profiles at lower panel from bottom to top: 0.604 molL^{-1} , 1.094 molL^{-1} and 2.208 molL^{-1} $\text{NaCH}_3\text{CO}_2(\text{aq})$. Note, that there is no narrow band at 3670 cm^{-1} in contrast to the $\text{NaCF}_3\text{CO}_2(\text{aq})$ detectable (see Figure S7).

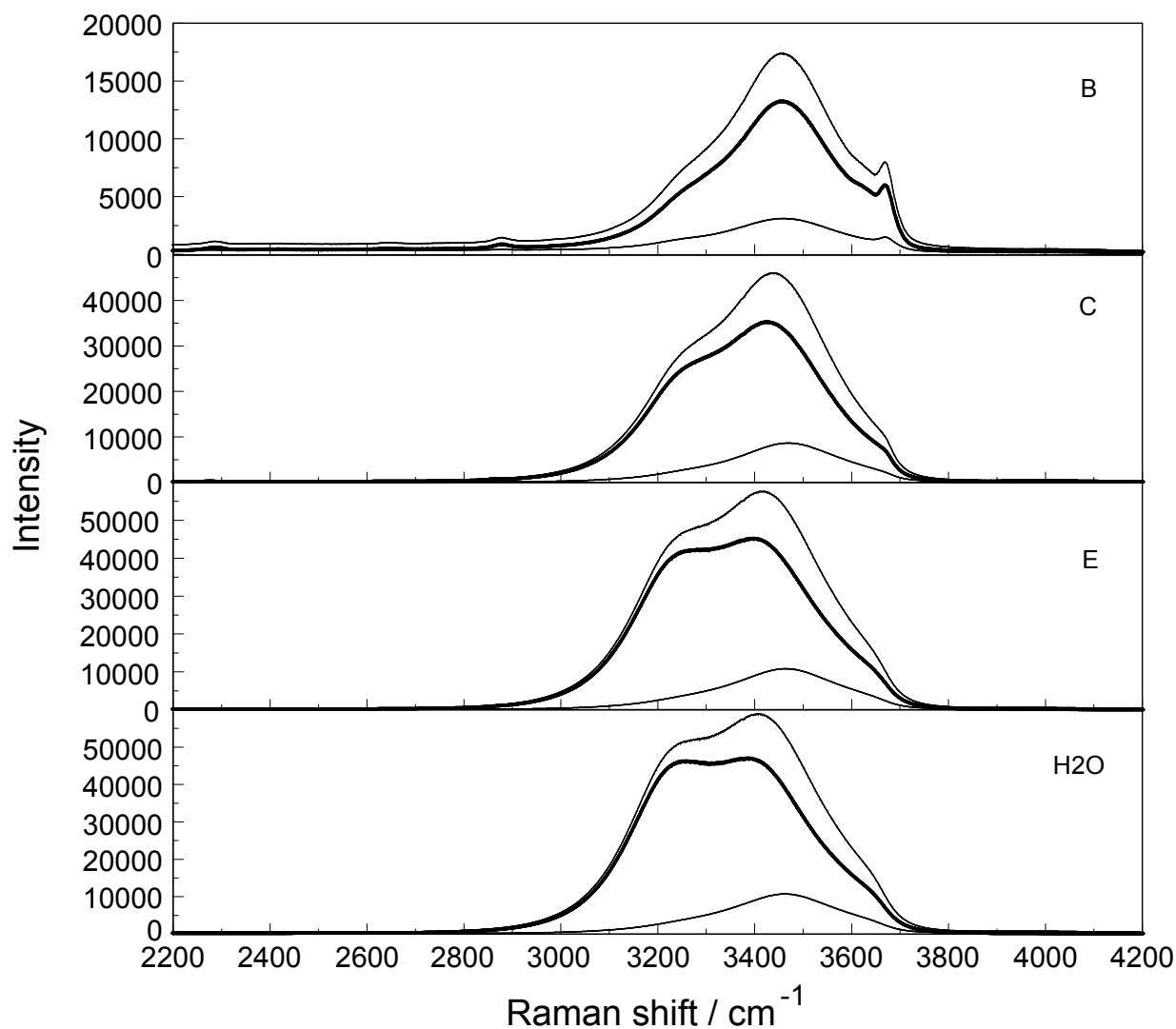


Figure S7. Raman scattering profiles of the O-H band region (polarized, depolarized and isotropic (thick black line)) of $\text{NaCF}_3\text{CO}_2(\text{aq})$ from 0 to 9.45 molL^{-1} . (From bottom to top: neat water, E) 0.850 molL^{-1} , C) 3.554 molL^{-1} , B) 9.45 molL^{-1} . Note the evolving narrow band at 3670 cm^{-1} in the $\text{CF}_3\text{CO}_2^-(\text{aq})$ scattering profiles.

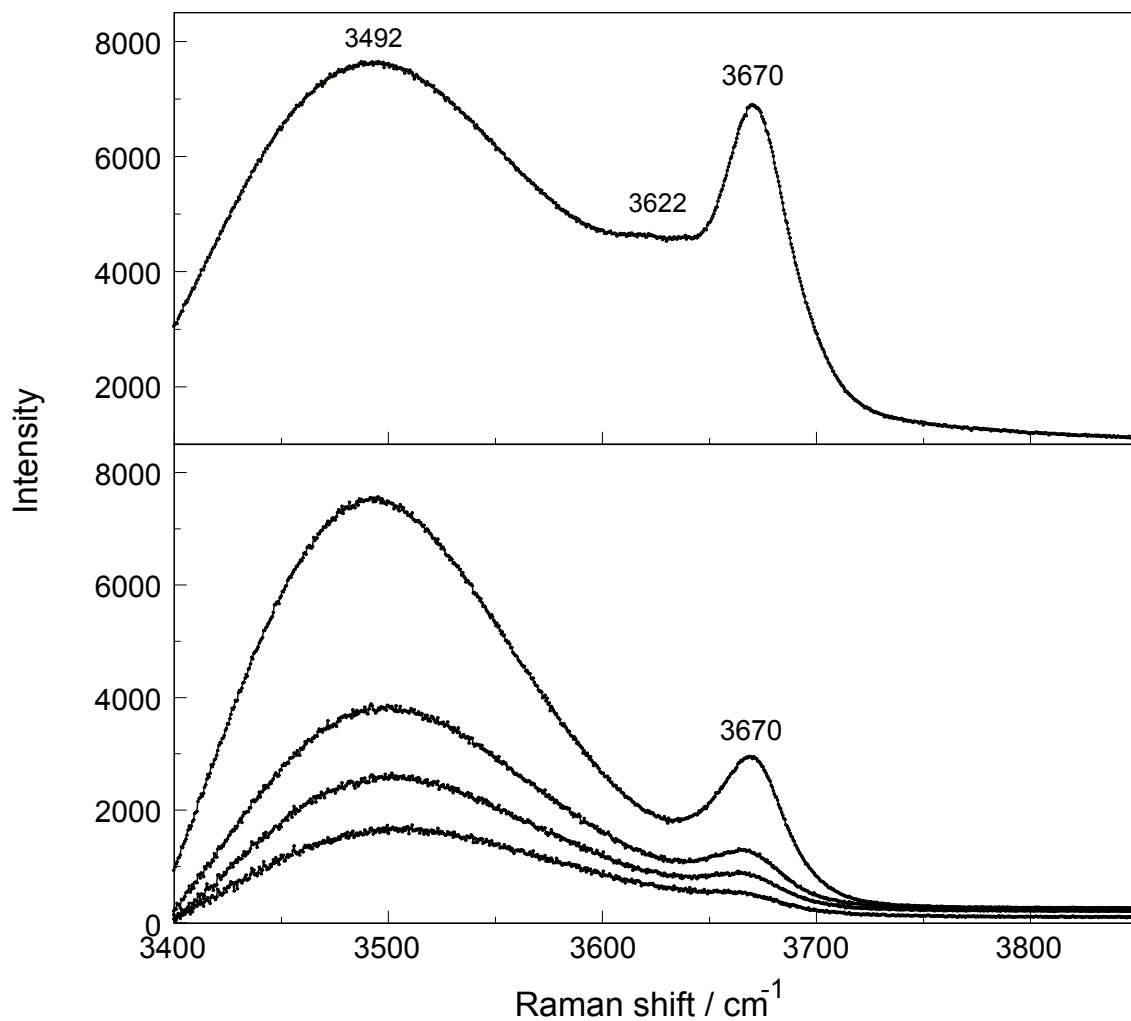


Figure S8. Raman difference spectra of the polarized O-H band region of $\text{NaCF}_3\text{CO}_2(\text{aq})$ from 0 to 9.45 molL^{-1} (see also Figure S6). The water band has been subtracted from each solute spectrum. Concentration profiles at lower panel from bottom to top: neat water, 0.427 molL^{-1} , 0.850 molL^{-1} ; 1.424 molL^{-1} and 3.554 molL^{-1} and upper panel hydrate melt 9.45 molL^{-1} . Note the evolving narrow band at 3670 cm^{-1} in the trifluoroacetate scattering profiles.