

# Vibrational Behavior of Calcium Hydrogen Triacetate Monohydrate, $\text{CaH}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$

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The IR and Raman spectra of calcium hydrogen triacetate monohydrate,  $\text{CaH}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ , (Speakman's classification: B type acid salt) in the 4000–400  $\text{cm}^{-1}$  frequency region are presented and discussed with respect to the fundamental vibrations of acetic acid species ( $\text{CH}_3\text{COO}^-$  and  $\text{CH}_3\text{COOH}$ ) and hydrogen bond vibrations due to both hydroxyl groups of  $\text{CH}_3\text{COOH}$  and water molecules. The main spectral feature in the  $\nu(\text{OH})$  stretching mode region is the appearance of two broad bands at about 2500 and 1950  $\text{cm}^{-1}$ , designated as (AB) and C bands, respectively. The presence of ABC bands with their frequency positions and intensities as well as the  $\delta_{\text{OH}}$  and  $\gamma_{\text{OH}}$  frequencies are spectroscopic evidence for strong asymmetrical hydrogen bonds between the acetic acid species. Their enthalpies of formation ( $\Delta H$ ) were calculated to be  $-48.4$  and  $-52.7$   $\text{kJ mol}^{-1}$ . Frequencies of the uncoupled OD stretches of the crystallization water reveal that  $\text{H}_2\text{O}(2)$  forms stronger hydrogen bonds than  $\text{H}_2\text{O}(1)$  and that the non-coordinated acetate oxygen is a stronger hydrogen bond acceptor than the carbonyl oxygen. The IR and Raman spectra of  $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  are also presented and discussed.

## INTRODUCTION

Vibrational spectra (IR and Raman) of a considerable number of acid salts of carboxylic acids of the general formula  $\text{MH}(\text{RCOO})_2$ , where  $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$ , have been well studied.<sup>1–6</sup> The great interest in these compounds is caused by their peculiar spectral characteristics in the  $\nu_{\text{OH}}$  stretching mode region, which are due to the presence of very strong hydrogen bonds in their crystal lattices. The dynamics of the hydrogen bond and the potential energy function of the proton of strongly hydrogen bonded systems are widely discussed in the literature<sup>7–9</sup> because of the great importance of the hydrogen bond formation for the physical properties of substances as well as for biological systems.<sup>6,10–12</sup>

The present paper aims at studying the vibrational spectra (IR and Raman) of calcium hydrogen triacetate monohydrate ( $\text{CaH}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ ), which is a repre-

sentative of B type acid carboxylic salts according to Speakman's classification. To our knowledge, no such data are available in the literature. The acid salt spectra are discussed with respect to the fundamental vibrations of the acetic acid species ( $\text{CH}_3\text{COO}^-$  and  $\text{CH}_3\text{COOH}$ ) and the hydrogen bond vibrations. A comparison is made with the vibrational spectra of the neutral salt, calcium acetate monohydrate, for which no full spectroscopic data are available.<sup>13,14</sup>

## EXPERIMENTAL

Acid and neutral calcium acetate monohydrates were prepared by crystallization from acid acetate solutions according to the solubility data of the  $\text{Ca}(\text{CH}_3\text{COO})_2 - \text{CH}_3\text{COOH} - \text{H}_2\text{O}$  system at 25 °C.<sup>15</sup> The crystals were filtered, washed with alcohol and dried in air. Deuterated samples contain-

ing about 10 and 40 % D<sub>2</sub>O (for the acid salt only) were obtained by the same crystallization procedures, using mixtures of H<sub>2</sub>O and D<sub>2</sub>O and 100 % D<sub>2</sub>O, respectively. Unfortunately, we failed to prepare more highly deuterated samples. The reagents used were of *p.a.* quality (Merck).

The IR spectra at ambient and liquid nitrogen temperature (LNT) were recorded on a Bruker model IFS 113 Fourier transform interferometer (resolution < 2 cm<sup>-1</sup>) using KBr as matrix. Ion exchange or other reactions with KBr were not observed. The Raman spectra (ambient temperature) of the samples in glass capillaries were measured on a RFS 100/S FT-Raman spectrometer using Nd:YAG laser excitation at 1064 nm (back – scattering geometry, resolution < 2 cm<sup>-1</sup>).

## RESULTS AND DISCUSSION

Both acid and neutral calcium acetate monohydrates, henceforth called CAHAC and CAAC, respectively, crystallize in the triclinic space group  $P\bar{1}$  ( $C_1$ ) with  $Z = 4$ .<sup>16,17</sup> Part of the crystal structure of CAHAC according to Ref. 16 is shown in Figure 1. Crystal structures of the two salts are very close. Both structures are built of infinite multiple O-bridged double-stranded Ca chains running in the *a* direction, which are cross-linked in the *b* and *c* directions *via* hydrogen bonds. Individual strands of the O-bridged Ca chains consist of the corresponding asymmetric units of the unit cells, namely Ca<sub>2</sub>H<sub>2</sub>(OAc)<sub>6</sub> · 2H<sub>2</sub>O and Ca<sub>2</sub>(OAc)<sub>4</sub> · 2H<sub>2</sub>O for the acid and neutral salts, respectively. Each unit cell contains four crystallographically different acetate ions, two calcium ions and two water molecules. Additionally, two acetic acid mol-

ecules are present in the acid salt lattice. All species in the two salts are in  $C_1$  site symmetry.

The factor group analysis predicts that under the  $C_1$  factor group symmetry and  $C_1$  site symmetry each vibrational mode (*A* symmetry) will give rise to only one IR-active component ( $A_u$  symmetry) and only one Raman-active component ( $A_g$  symmetry).

### Vibrations of CH<sub>3</sub>COO<sup>-</sup> and CH<sub>3</sub>COOH Species in CAHAC and CAAC

As regards crystallographic symmetry conditions, Speakman differentiates two fundamental types of acid salts of carboxylic acids – A and B.<sup>18</sup> In type A, the two carboxylic residues (RCOO<sup>-</sup> and RCOOH) are equivalent and the hydrogen bond lies across the symmetry centre (symmetric hydrogen bonds). A large number of alkali acid salts of acetic and halogenated acetic acids is reported to belong to type A – for example, NaH(CH<sub>3</sub>COO)<sub>2</sub>,<sup>19</sup> KH(CF(Cl)<sub>3</sub>COO)<sub>2</sub>,<sup>3,20</sup> KH(CHBr<sub>2</sub>COO)<sub>2</sub>,<sup>5</sup> RbH(CCl<sub>3</sub>COO)<sub>2</sub>,<sup>21</sup> *etc.* Type B corresponds to asymmetric hydrogen bonds, *i.e.*, the C–O distances and OCO angles show clearly distinct COOH carboxylic and COO<sup>-</sup> carboxylate groups of the complex anion (RCOOHOOCR). To our knowledge, few of the studied acid carboxylic salts belong to type B – for example, potassium hydrogen phthalate (KHPH),<sup>22</sup> NaHC<sub>2</sub>O<sub>4</sub> · H<sub>2</sub>O,<sup>23</sup> NaHC<sub>2</sub>O<sub>4</sub>,<sup>24</sup> β-potassium hydrogen hydroxymalonate.<sup>25</sup>

According to the structural data, CAHAC is a type B acid salt. Vibrational spectra of type B salts are interpreted roughly in terms of superposition of RCOOH and RCOO<sup>-</sup> bands, taking into account both the dimensions and the type of bonding of the two residues obtained by

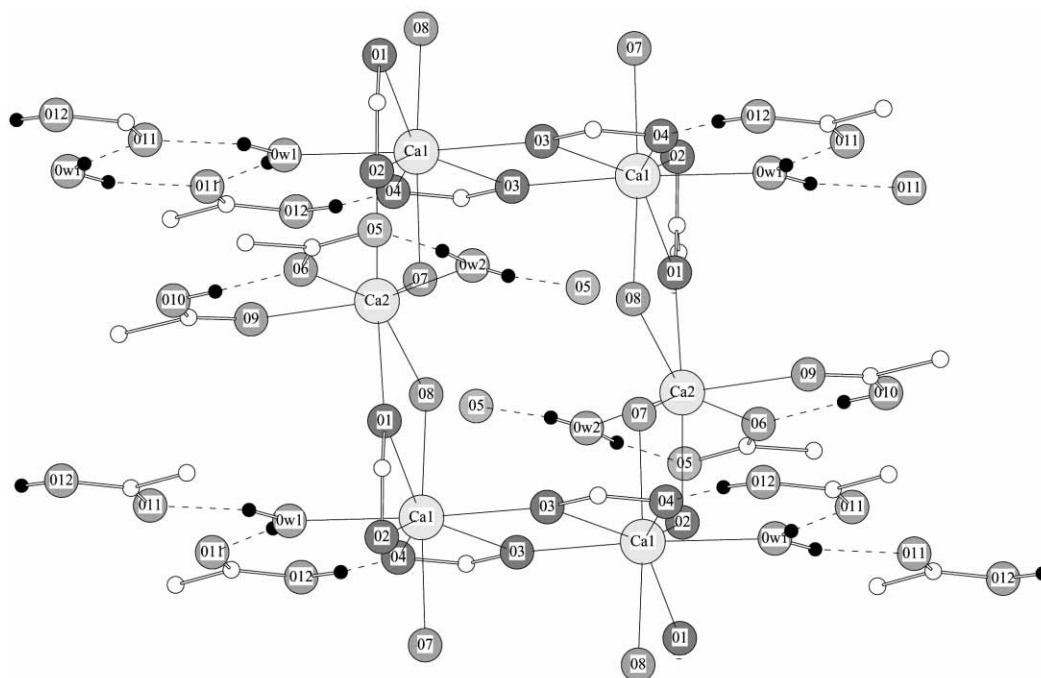


Figure 1. Part of the crystal structure of CaH(CH<sub>3</sub>COO)<sub>3</sub> · H<sub>2</sub>O according to data from Ref. 16; (● are H atoms; ○ are C atoms).

Table I. Assignments of the bands, corresponding to the vibrations of OAc and AcOH, in the vibrational spectra of CAHAC and CAAC (data in parentheses are for the deuterated sample; only bands affected by the deuteration are mentioned)

CAHAC			CAAC			Assignments
IR / $\text{cm}^{-1}$		Raman / $\text{cm}^{-1}$	IR / $\text{cm}^{-1}$		Raman / $\text{cm}^{-1}$	
295 K	90 K	295 K	295 K	90 K	295 K	
3020	3016	3027 sh	3010	3007	3017	$\nu_{\text{as}}(\text{CH}_3)$
		2998		2984	2983	$\nu'_{\text{as}}(\text{CH}_3)$
2926	2918	2941	2926	2924	2932	$\nu_{\text{s}}(\text{CH}_3)$
1700	1702 (1702)	1697 (1684)	–	–	–	$\nu(\text{C}=\text{O})$ of AcOH
1684 sh	1684 (1670)					
1615 sh	1612	1580	1583	1587	1580	$\nu_{\text{as}}(\text{C}-\text{O})$ of OAc
1551	1554		1565	1567		
	1530 sh		1545	1545		
1475	1483					$\delta_{\text{as}}(\text{CH}_3)$ or $\nu_{\text{s}}(\text{C}-\text{O})$ of OAc
1454	1460	1468	1460 sh	1469	1475	$\nu_{\text{s}}(\text{C}-\text{O})$ of OAc
			1450	1455		
1414	1433	1434	1415	1425	1437	$\delta'_{\text{as}}(\text{CH}_3)$
	1415	1413 sh		1413	1417	
	1408 sh			1399		
1370 (1126)	1391 (1130)	(1126)	–	–	–	$\delta_{\text{OH}}$ of AcOH
(1099)	1369 (1107)	(1095)				
1349	1349	1357	1355	1355	1364	$\delta_{\text{s}}(\text{CH}_3)$
1335	1337	1347	1341	1339	1348	
		1341				
1302	1315	1314 (1325)	–	–	–	$\nu(\text{C}-\text{O})$ of AcOH
	1304					
	1099 (780)		–	–	–	$\gamma_{\text{OH}}$ of AcOH
	1070 (765)					
1052	1055		1057	1058		$\rho_{\text{op}}(\text{CH}_3)$
	1052			1049		
	1047					
1026	1031	1020	1024	1029	1020	$\rho_{\text{ip}}(\text{CH}_3)$
1019	1017			1024		
962	965	960	961	966	965	$\nu(\text{C}-\text{C})$ of OAc
951	958	955	945	948	946	
941	953	943	932	944	943	
	942			931	931	
901 (865)	906 (875)	903 (872)	–	–	–	$\nu(\text{C}-\text{C})$ of AcOH
	901					
688	693	688				$\delta_{\text{s}}(\text{OCO})$ and/or twisting vibration
672	674	668	677	678	686	$\delta(\text{OCO})$
663	664	664	661	661	672	
					660	
636	640	638	623	622	642	$\rho_{\text{op}}(\text{OCO})$ of OAc and $\delta(\text{OCO})$ +
620	627	628 sh	617	613	620	$\gamma(\text{CCO})$ of AcOH
	620 sh	618				
	610	610				
464	463	476	480	482	480	$\rho_{\text{ip}}(\text{OCO})$ of OAc and $\delta(\text{CCO})$ of AcOH
		460	473	468	466	

the structural data.<sup>3</sup> In the CAHAC lattice, one of the OAc ions is a monodentate ligand, while the others act as bidentate chelating and O-bridging ligands. The C-O bond lengths in the OAc ions, which are in the range 1.24–1.27 Å, are close to those found in other metal acetates.<sup>26–28</sup> The two C-O bond lengths in each AcOH molecule differ significantly – they are about 1.2 and 1.3 Å for the short (C=O) and the long bond (C-O), respectively, and are thus close to those found in solid acetic acid.<sup>29</sup> The carbonyl group of one AcOH, denoted as AcOH(1), is coordinated to Ca(2) and its OH group is involved in a hydrogen bond with an acetate oxygen O(6) (Figure 1). The other AcOH, named AcOH(2), is non-coordinated, but it is extensively involved in the hydrogen bond network of the salt by three hydrogen bonds with the acetate oxygen O(4) (as proton donor) and two water molecules (as proton acceptors) (Figure 1).

As far as the neutral salt, CAAC, is concerned, the four non-equivalent acetate ions are bonded in its lattice<sup>17</sup> in a manner similar to that found in CAHAC,<sup>16</sup> *i.e.*, one OAc ion is a monodentate ligand, while the others are both bidentate chelating and O-bridging ligands.

The 15 fundamental modes of the (OAc) ions and the 18 fundamentals of AcOH are well studied in the literature.<sup>29–31</sup> In the case of more than one OAc ion and more than one AcOH molecule in the lattice, more sets of fun-

damental modes are expected to occur, corresponding to the number of the crystallographically different species of each type.

The infrared and Raman spectra of CAHAC and CAAC in the region of 1800–400 cm<sup>-1</sup> are shown in Figures 2–4 and the assignments of the bands are given in Table I. The assignments are based on the literature data for neutral carboxylic salts<sup>30,31</sup> and different acid salts of carboxylic acids.<sup>4,5,21–24,29</sup>

The presence of four different acetate ions, bonded in a similar manner in both salts, results in close vibrational characteristics in the regions of stretching and bending vibrations of OCO groups, C-C stretching and methyl group vibrations, which can be seen from Figures 2–4 and Table I.

As it could be expected, the main difference in the vibrational spectra of the acid and the neutral salts in the region of 1800–400 cm<sup>-1</sup> is the appearance of bands corresponding to the vibrations of COOH groups of the acetic acid molecules, namely – carbonyl (C=O) and C-O stretching vibrations as well as hydroxyl group vibrations (in-plane ( $\delta_{OH}$ ) and out-of-plane ( $\gamma_{OH}$ ) bending vibrations).

The carbonyl stretching vibration is observed in the IR spectrum of CAHAC as a strong band with two maxima at 1702 and 1684 cm<sup>-1</sup> (LNT), corresponding to the two carbonyl groups of the two acetic acid molecules (Figure 2a and 2b). The lower wavenumbered  $\nu_{C=O}$  band shifts to a lower frequency (1670 cm<sup>-1</sup>) on deuteration (Figure 2d), which is caused by the reduction of the interaction with some protonic modes, possibly the bending mode of water molecules. As mentioned above, according to the structural data, only the carbonyl group of AcOH(2) is an acceptor of two hydrogen bonds with two water molecules. Logically, the  $\nu_{C=O}$  vibration of AcOH(2) should be sensitive to the close lying  $\delta_{H_2O}$  vibrations of the water molecules and affected by the deuteration. Based on the above consideration, we assume that the band at 1684 cm<sup>-1</sup> is due to  $\nu_{C=O}$  of AcOH(2), while the higher frequency band at 1702 cm<sup>-1</sup> is due to AcOH(1). In the Raman spectrum, only one band at 1697 cm<sup>-1</sup> appears, which also shifts to a lower frequency on deuteration (Figure 4a and 4b).

The other spectral region, which is very characteristic of acid carboxylic salts is the region of 1420–1250 cm<sup>-1</sup>, where coupled vibrations involving  $\delta_{OH}$  and  $\nu_{C-O}$  appear.<sup>1,4,22,23,32,33</sup> Comparison of curves (a) and (e) in Figure 2 clearly shows that two new strong bands at 1370 and 1302 cm<sup>-1</sup> appear in the IR spectrum of CAHAC at ambient temperature, which are absent in that of CAAC. In agreement with the literature data, the lower frequency band (at 1302 cm<sup>-1</sup>) should have a predominantly  $\nu_{C-O}$  character. At cooling, the  $\nu_{C-O}$  mode splits into two bands (1315 and 1304 cm<sup>-1</sup>) corresponding to the two C-O bonds (1.302 and 1.324 Å) of the two acetic

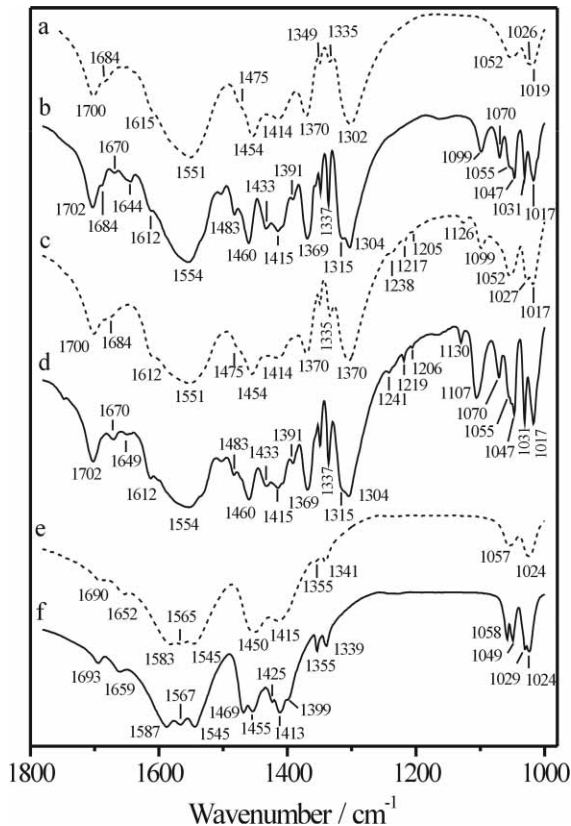


Figure 2. IR spectra in the 1800–1000 cm<sup>-1</sup> frequency region of (a, b) CAHAC; (c, d) deuterated (40 % D<sub>2</sub>O) CADAC; (e, f) CAAC; (--- at ambient temperature; — at liquid nitrogen temperature).



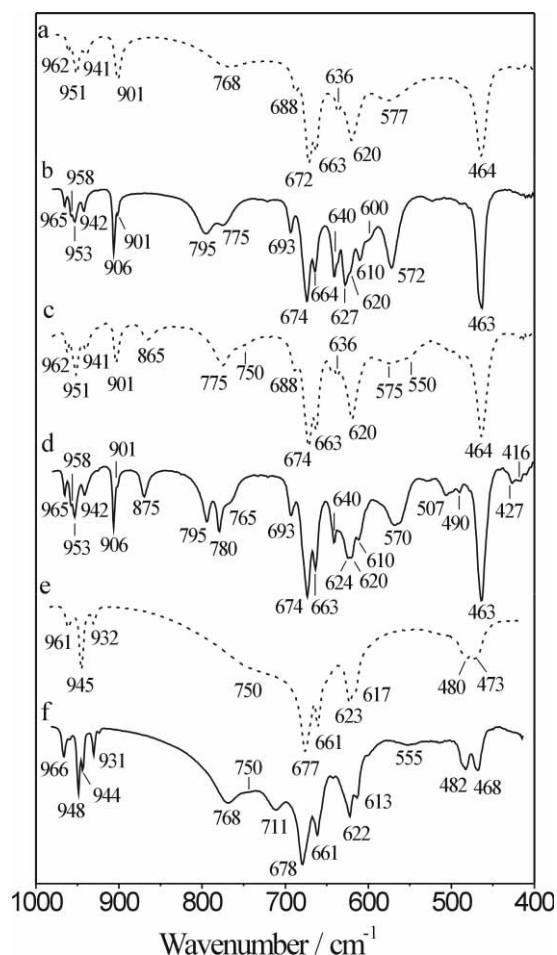


Figure 3. IR spectra in the 1000–400  $\text{cm}^{-1}$  frequency region of (a, b) CAHAC; (c, d) deuterated (40 %  $\text{D}_2\text{O}$ ) CADAC; (e, f) CAAC; (--- at ambient temperature; — at liquid nitrogen temperature).

acid molecules. On deuteration, a shift to higher frequencies of the  $\nu_{\text{C-O}}$  mode is expected to occur as a result of removing the coupling with  $\delta_{\text{OH}}$ .<sup>19,29–33</sup> In the spectrum of 40 % deuterated sample, no shift was measured (compare curves (b) and (d) in Figure 2). However, in the Raman spectrum the singlet band at 1314  $\text{cm}^{-1}$ , assigned to the  $\nu_{\text{C-O}}$  mode, exhibits an upshift to 1325  $\text{cm}^{-1}$  on deuteration (Figure 4a and 4b and Table I).

The band having most of the  $\delta_{\text{OH}}$  character appears at about 1400  $\text{cm}^{-1}$  in IR spectra of carboxylic dimers and adducts<sup>29,33–35</sup> and at even higher frequencies in some acid salts.<sup>5,7,21,32</sup> It is claimed<sup>29,32</sup> that  $\delta_{\text{OH}}$  frequency increases with increasing the hydrogen bond strength and as a result an upshift of this mode is expected to be observed at LNT. In most cases, identification of the  $\delta_{\text{OH}}$  mode is complicated because of the presence of a considerable number of bands in the region.<sup>4,5,19,22,36</sup> However, a pure  $\delta_{\text{OD}}$  vibration is observed in the 1050–1170  $\text{cm}^{-1}$  frequency region in the deuterated sample.<sup>4,5,20,22,33</sup> In the IR spectrum of CAHAC, at ambient temperature we assign the band at 1370  $\text{cm}^{-1}$  to the  $\delta_{\text{OH}}$  mode. At LNT, a new band with a considerably lower intensity appears

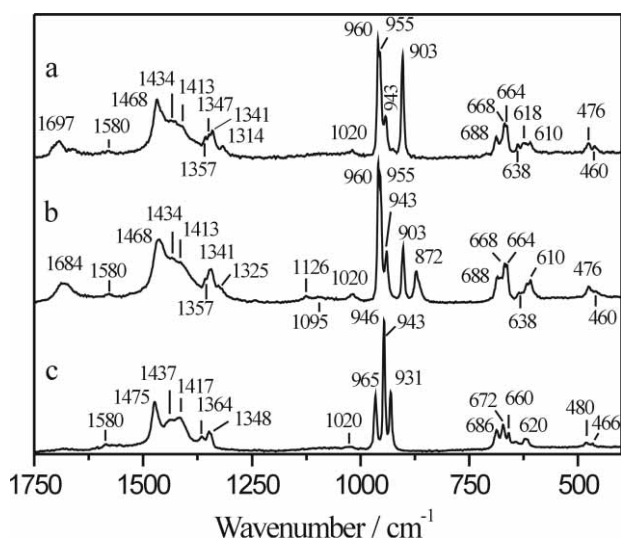


Figure 4. Raman spectra in the 1800–400  $\text{cm}^{-1}$  frequency region of (a) CAHAC; (b) deuterated (40 %  $\text{D}_2\text{O}$ ) CADAC; (c) CAAC.

at 1391  $\text{cm}^{-1}$  (Figure 2a and 2b). This band could be attributed either to  $\delta_{\text{as}}'(\text{CH}_3)$  or to the second  $\delta_{\text{OH}}$  mode. Further, in the IR spectrum of the 40 % deuterated sample (Figure 2c) two well defined bands appear at 1126 and 1099  $\text{cm}^{-1}$ , exhibiting an upshift at LNT (1130 and 1107  $\text{cm}^{-1}$ , respectively) and they are attributed to  $\delta_{\text{OD}}$  modes of the two acetic acid molecules. As seen from Figure 2c, the higher wavenumbered  $\delta_{\text{OD}}$  band has a considerably lower intensity compared to that of the lower wavenumbered one, like in the case of the protonated sample. On this basis we assume that the band at 1391  $\text{cm}^{-1}$  in IR spectrum of CAHAC at LNT is more likely to be the second  $\delta_{\text{OH}}$  mode. In this case, the isotopic shift for the two  $\delta_{\text{OH}}$  bands is 1.23–1.24, which coincides with the reported one.<sup>32</sup> In the Raman spectrum of CAHAC, no bands attributed to  $\delta_{\text{OH}}$  mode could be seen, but in the deuterated sample two very weak bands at 1126 and 1095  $\text{cm}^{-1}$  assigned to the  $\delta_{\text{OD}}$  vibrations are observed (Figure 4b).

According to the literature data, the out-of-plane bending vibration ( $\gamma_{\text{OH}}$ ) is in fact characteristic of hydrogen bonded acetic acid, since it is not found in the monomer. The frequency position of  $\gamma_{\text{OH}}$  is too sensitive towards molecular interactions and can be used as a criterion of the hydrogen bond strength.<sup>38</sup> Thus, the shortening of the hydrogen bond length from 2.61 Å found in solid acetic acid to about 2.52–2.57 Å in type B salts increases the  $\gamma_{\text{OH}}$  frequency from 906  $\text{cm}^{-1}$  to 1040–1140  $\text{cm}^{-1}$ .<sup>23,30,38</sup> For very strong hydrogen bonds with O...O distances of 2.43–2.47 Å found in type A salts, the  $\gamma_{\text{OH}}$  band appears around 1200  $\text{cm}^{-1}$ .<sup>4,21,38</sup> The  $\gamma_{\text{OH}}$  vibration usually appears as a relatively narrow band with a remarkable shift to higher frequencies (up to 25  $\text{cm}^{-1}$ ) on cooling and a high isotopic shift about 1.35–1.40 Å on deuteration.<sup>38</sup> In the IR spectrum of CAHAC, at ambient temperature

we did not find a band or bands with appropriate characteristics of this mode. However, at LNT two relatively narrow bands with equal intensities appear at 1070 and 1099  $\text{cm}^{-1}$ , which are assigned to  $\gamma_{\text{OH}}$  of the two AcOH molecules (Figure 2b). Taking into account the upshift at cooling, we suppose that at ambient temperature the  $\gamma_{\text{OH}}$  bands should appear at about 1050  $\text{cm}^{-1}$ , thus overlapping with the bands due to the out-of-plane  $\text{CH}_3$  rocking vibrations (see Table I). On deuteration, the corresponding  $\gamma_{\text{OD}}$  modes are expected to occur in the region of 780–740  $\text{cm}^{-1}$ . However, identification of the  $\gamma_{\text{OD}}$  modes is complicated since our sample is only 40 % deuterated. As a result, both the rocking vibrations of  $\text{H}_2\text{O}$  and the  $\gamma_{\text{OD}}$  vibrations of AcOD appear in this spectral range. Comparison of the IR spectra of protonated and deuterated samples at ambient temperature (Figure 3a and 3c) shows that the broad shoulder at about 750  $\text{cm}^{-1}$  could be assigned to the  $\gamma_{\text{OD}}$  mode with an isotopic ratio of 1.38. This means that the  $\gamma_{\text{OH}}$  mode shows almost pure harmonic behaviour. When the corresponding spectra at LNT are compared (Figure 3b and 3d), it is seen that the intensity of the band at 780  $\text{cm}^{-1}$  increases considerably on deuteration compared to that of the band at 795  $\text{cm}^{-1}$ . Since in the IR spectrum of the protonated sample these two bands originate from the rocking vibrations of the  $\text{H}_2\text{O}$  molecules (see discussion below), the above commented fact could be explained by the assumption that the second  $\gamma_{\text{OD}}$  mode appears at 780  $\text{cm}^{-1}$ , thus overlapping with the rocking vibrations of the second  $\text{H}_2\text{O}$  molecule.

The  $\gamma_{\text{OH}}$  frequency can be related to the hydrogen bond energy (enthalpy of hydrogen bond formation) by the equation given below, established for the crystalline acid carboxylic salts,<sup>39</sup> providing that the hydrogen bonds are linear (as in CAHAC):<sup>16</sup>

$$-\Delta H = 0.67 \times 10^{-4} [(v_{\text{H}})^2 - (v_{\text{O}})^2],$$

where  $\Delta H$  is in  $\text{kJ mol}^{-1}$  (the accuracy is estimated<sup>39</sup> to be within 4  $\text{kJ mol}^{-1}$ ). In the equation,  $v_{\text{H}}$  and  $v_{\text{O}}$  are the  $\gamma_{\text{OH}}$  frequency ( $\text{cm}^{-1}$ ) of hydrogen bonded and free molecule (650  $\text{cm}^{-1}$  for  $\text{CH}_3\text{COOH}$  monomer),<sup>38</sup> respectively. Calculated values for  $\Delta H$  of the two hydrogen bonds formed by the hydroxyl groups of the two acetic acid molecules are 48.4 and 52.7  $\text{kJ mol}^{-1}$ , respectively, thus indicating the formation of strong hydrogen bonds in CAHAC.

As far as the C-C mode is concerned, four bands corresponding to the four acetate ions present in the crystal lattice of both acid and neutral salts, appear in the IR (LNT) and Raman (ambient temperature) spectra in the region of 965–930  $\text{cm}^{-1}$  (Figures 3 and 4, Table I). Additionally, one or two bands around 900  $\text{cm}^{-1}$  are observed both in the IR and Raman spectra of the acid salt only (Figure 3a and b, Figure 4a) and, in agreement with

the literature data,<sup>29</sup> they are assigned to the  $\nu_{\text{C-C}}$  mode of AcOH molecules. The  $\nu_{\text{C-C}}$  mode in AcOH is shown to be strongly perturbed by both  $\gamma_{\text{OH}}$  and out-of-plane  $\text{CH}_3$  rocking vibrations and shows a considerable downshift (to 35  $\text{cm}^{-1}$ ) on deuteration.<sup>5,29,37</sup> Comparison of the IR and Raman spectra of protonated and deuterated samples shows that the intensity of the band at around 900  $\text{cm}^{-1}$  decreases nearly twice on deuteration and at the same time a new band appears at 865  $\text{cm}^{-1}$  in the IR spectrum and at 872  $\text{cm}^{-1}$  in the Raman spectrum (Figure 3c and Figure 4b). The latter is attributed to the unperturbed  $\nu_{\text{C-C}}$  mode of the acetic acid molecules.

### Hydrogen Bond Vibrations in $\text{CaH}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$

*Crystal Structure Data.* – According to the structural data,<sup>16</sup> six different hydrogen bonds exist in the lattice of the acid salt. Two of them, the shortest ones (O...O distances of about 2.55 Å) are formed by the hydroxyl groups of the two acetic acid molecules and the longest ones (O...O distances from 2.73 to 2.88 Å) are formed by the two water molecules. The hydrogen bonds scheme is shown in Figure 1 and some structural data necessary for the IR spectra interpretations are summarized in Table II.

The AcOH (1) molecule is coordinated to the Ca(2) ion and is the proton donor in one hydrogen bond with the acetate oxygen O(6), the latter bonded to the same Ca(2) ion. The non-coordinated AcOH(2) is involved in three hydrogen bonds – one short hydrogen bond with the acetate oxygen O(4) being the proton donor and two longer hydrogen bonds with two different  $\text{H}_2\text{O}$ (1) molecules as proton acceptors (by the carbonyl oxygen O(11)). Both  $\text{H}_2\text{O}$ (1) and  $\text{H}_2\text{O}$ (2) are coordinated to Ca(1) and Ca(2), respectively, with practically equal Ca-O<sub>w</sub> bond lengths (Table II) and both act as proton donors only.  $\text{H}_2\text{O}$ (1) forms hydrogen bonds with the carbonyl oxygen O(11) of two AcOH(2) molecules, while  $\text{H}_2\text{O}$ (2) with the non-coordinated acetate oxygen O(5) of the two different acetate ions. With respect to the O...O distances,  $\text{H}_2\text{O}$ (1) shows weaker hydrogen bonds compared to those of  $\text{H}_2\text{O}$ (2). Vibrations due to the crystallization water and OH groups of AcOH will be discussed separately.

*Vibrations of Crystallization Water.* – The IR spectra of CAHAC in the region of 4000–1800  $\text{cm}^{-1}$  are presented in Figure 5. Taking into consideration the O...O distances and the equal Ca-O<sub>w</sub> interactions (equal synergistic effect), the OH stretching modes of  $\text{H}_2\text{O}$ (1) are expected to appear at higher frequencies (weaker hydrogen bonds) than those of the  $\text{H}_2\text{O}$ (2) molecules. Bands at 3517 and 3448  $\text{cm}^{-1}$  (spectrum at LNT) are thus assigned to asymmetric and symmetric stretching vibrations of  $\text{H}_2\text{O}$ (1), respectively, while the bands at 3228 and 3110  $\text{cm}^{-1}$  – to the OH stretches of  $\text{H}_2\text{O}$ (2) (Figure 5b). Frequency separation between the average values of the OH stretching

Table II. Some structural data for  $\text{CaH}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ 

Substance	Proton donors	Hydrogen bond type	O...O	O-H...O	Ca-O <sub>w</sub>	
			distance / Å	angle / deg		bond length / Å
CAHAC	AcOH(1)	O(10)-H(1)...O(6) <sup>(a)</sup>	2.548	176	2.372	
	AcOH(2)	O(12)-H(2)...O(4) <sup>(a)</sup>	2.550	175		
	H <sub>2</sub> O(1)	O <sub>w</sub> (1)-H(11)...O(11) <sup>(a)</sup>	2.864	179		
		O <sub>w</sub> (1)-H(12)...O(11 <sup>iv</sup> ) <sup>(a)</sup>	2.876	162		
	H <sub>2</sub> O(2)	O <sub>w</sub> (2)-H(21)...O(5) <sup>(a)</sup>	2.732	166		2.375
		O <sub>w</sub> (2)-H(22)...O(5 <sup>v</sup> ) <sup>(a)</sup>	2.750	152		
CAAC	H <sub>2</sub> O(1)	O <sub>w</sub> (1)-H(11)...O(6 <sup>ii</sup> ) <sup>(b)</sup>	2.742	173	2.360	
		O <sub>w</sub> (1)-H(12)...O(3 <sup>v</sup> ) <sup>(b)</sup>	2.803	166		
	H <sub>2</sub> O(2)	O <sub>w</sub> (2)-H(21)...O(6 <sup>iv</sup> ) <sup>(b)</sup>	2.699	166		2.368
		O <sub>w</sub> (2)-H(22)...O(6 <sup>ii</sup> ) <sup>(b)</sup>	2.994	153		

<sup>(a)</sup> O(4), O(5) and O(6) are oxygens from acetate ions; O(11) is carbonyl oxygen (C=O) of AcOH(2)

<sup>(b)</sup> O(6) and O(3) are oxygen from acetate ions

vibrations of the two water molecules is about  $320 \text{ cm}^{-1}$ , indicating a significant difference in the strength of the hydrogen bonds formed by H<sub>2</sub>O(1) and H<sub>2</sub>O(2). The bending modes of the two water molecules are only seen in the spectrum at LNT at  $1670$  and  $1644 \text{ cm}^{-1}$  (Figure 2b). Correspondingly, the weak bands at  $3390$  and  $3280 \text{ cm}^{-1}$  are probably due to the overtone  $2\delta_{\text{H}_2\text{O}}$  of the water molecules.

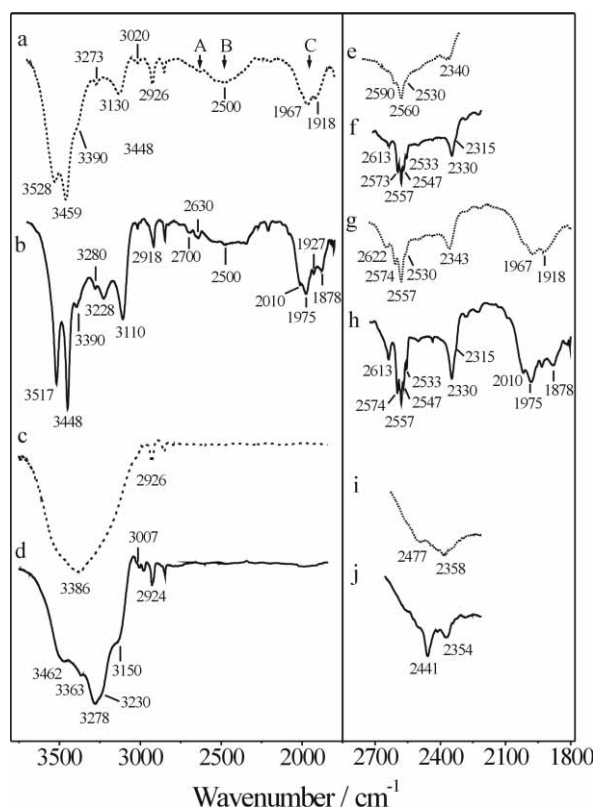


Figure 5. IR spectra in the  $4000\text{--}1800 \text{ cm}^{-1}$  frequency region of (a, b) CAHAC; (c, d) CAAC; (e, f) deuterated ( $10\% \text{ D}_2\text{O}$ ) CAHAC; (g, h) deuterated ( $40\% \text{ D}_2\text{O}$ ) CADAC; (i, j) deuterated ( $10\% \text{ D}_2\text{O}$ ) CAAC (--- at ambient temperature; — at liquid nitrogen temperature).

In accordance with the structural data, four uncoupled OD modes, corresponding to the four different hydrogen bond lengths (Table II), are expected to be observed in the IR spectrum of the isotopically diluted sample (up to  $10\% \text{ D}_2\text{O}$ ). As seen from Figure 5e, a band at  $2340 \text{ cm}^{-1}$  and three bands at higher frequencies, namely at  $2590$  (shoulder),  $2560$  and  $2530$  (shoulder)  $\text{cm}^{-1}$ , appear in the IR spectrum of the isotopically diluted sample at ambient temperature. The temperature decrease results in an increased number of bands observed in the OD stretching mode region. The band at  $2340 \text{ cm}^{-1}$  transforms into two bands at  $2330$  and  $2315$  (shoulder)  $\text{cm}^{-1}$  while the three bands in the region of  $2590\text{--}2530 \text{ cm}^{-1}$  split into four sharp bands at  $2533$ ,  $2547$ ,  $2557$  and  $2573 \text{ cm}^{-1}$  (Figure 5f). A band at  $2613 \text{ cm}^{-1}$ , weaker and broader than the other bands in the region, is also seen. Taking into account that H<sub>2</sub>O(2) forms stronger hydrogen bonds than H<sub>2</sub>O(1) we assign the bands at  $2330$  and  $2315 \text{ cm}^{-1}$  to H<sub>2</sub>O(2) and they correspond to hydrogen bond lengths of  $2.750$  and  $2.732 \text{ Å}$ , respectively. Then, the higher wavenumbered OD bands, most probably those in the range of  $2590\text{--}2530 \text{ cm}^{-1}$ , should be attributed to H<sub>2</sub>O(1). Obviously, the number of the OD bands observed for H<sub>2</sub>O(1) (three and four bands at ambient and liquid nitrogen temperatures, respectively) is larger than the two bands expected from the structural data. Two possible explanations of this fact could be proposed. The first is based on the assumption that H<sub>2</sub>O(1) molecules are orientationally disordered both at ambient and liquid nitrogen temperatures, but the structure becomes more ordered at LNT, which is shown by the small half-width of the bands ( $5\text{--}8 \text{ cm}^{-1}$ ). In the case of orientational disorder, distinct OD modes should be observed for each position occupied by disordered hydrogen atoms, as it has been established by both spectroscopic and X-ray diffraction studies of  $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$  at ambient and liquid nitrogen temperatures.<sup>40,41</sup> The other reason, discussed in the literature, resulting in an increase in the num-



ber of crystallographically non-equivalent protons, might be protonic order-disorder phase transition (second order type). Structural changes during these phase transitions are associated with a loss of symmetry element and thus the number of the crystallographically different water molecules increases. For example,  $K_4Fe(CN)_6 \cdot 3H_2O$  is known to undergo phase transition from paraelectric (SG  $C_{2h}^6$ ) to ferroelectric form (SG  $C_s^4$ ) at 249 K (Curie temperature,  $T_c$ ).<sup>42</sup> Above  $T_c$  there are two kinds of water molecules. Below  $T_c$  the inversion centre of the lattice is lost and the set of  $H_2O(2)$  molecules splits into non-equivalent groups –  $H_2O(2)$  and  $H_2O(3)$ , which results in an increase in the number of the OH bands observed in the IR and Raman spectra.<sup>42</sup> Using adiabatic calorimetry and IR spectroscopy, White and Falk have established that order-disorder phase transition occurs in  $Me(ClO_4)_2 \cdot 6H_2O$  ( $Me = Mg, Cd$ ) at 10 K, related to the increase in the number of distinguishable types of water protons.<sup>43</sup> Thus, one OD mode is observed in the IR spectra of the two salts at ambient temperature (one type symmetric water molecule), while 16 and 5 OD bands are observed in the IR spectra of  $Mg(ClO_4)_2 \cdot 6H_2O$  and  $Cd(ClO_4)_2 \cdot 6H_2O$ , respectively, at 10 K. In both cases (orientational disorder and second order type phase transition), the number of bending vibrations of the  $H_2O$  molecules should increase.<sup>40,43</sup> As commented above, two  $\delta_{H_2O}$  modes are identified in the IR spectrum of CAHAC at LNT. However, in the IR spectrum of the deuterated sample (40 %  $D_2O$ ), three bands at 1205, 1217 and 1238  $cm^{-1}$ , which fall in the region free from other vibrations, are clearly seen at ambient temperature (Figure 2c). They exhibit appropriate both isotopic (1.33–1.35) and temperature shifts (Figure 2d) and may be attributed to  $\delta_{D_2O}$  of water molecules. However, the assumptions made by us for CAHAC need additional studies, especially neutron diffraction studies at ambient and liquid nitrogen temperatures. Since these data are lacking, the IR spectra in this region, especially at LNT, could not be discussed in detail.

Some additional information could be derived if we compare the average values of the  $\nu_{OD}$  modes observed for  $H_2O(1)$  ( $\bar{\nu}_{exp}$  is 2557  $cm^{-1}$ ) and  $H_2O(2)$  ( $\bar{\nu}_{exp}$  is 2322  $cm^{-1}$ ), corresponding to the average  $O_w \cdots O$  distances of 2.87 and 2.74 Å, respectively, with the  $\nu_{OD}$  values calculated according to Mikenda's correlation curve<sup>44</sup> (uncoupled  $\nu_{OD}$  modes versus  $O \cdots O$  distances) for the same hydrogen bond lengths. The values thus calculated are:  $\bar{\nu}_{calc}$  about 2500  $cm^{-1}$  for  $H_2O(1)$  and  $\bar{\nu}_{calc}$  about 2400  $cm^{-1}$  for  $H_2O(2)$ . Deviations of the experimental  $\bar{\nu}_{exp}$  values from the calculated ones ( $\Delta\nu_{OD} = \bar{\nu}_{exp} - \bar{\nu}_{calc}$ ) are:  $\Delta\nu_{OD} = +57$   $cm^{-1}$  (above Mikenda's curve) and  $\Delta\nu_{OD} = -78$   $cm^{-1}$  (below Mikenda's curve) for  $H_2O(1)$  and  $H_2O(2)$ , respectively. In our opinion, these findings evidence that the non-coordinated acetate oxygen O(5) is a stronger hydrogen bond acceptor than the carbonyl oxygen O(11) of AcOH(2).

Two sets of water librations (rocking, twisting, wagging) are expected to appear in the IR spectrum of CAHAC, corresponding to the two types of water molecules in the lattice. Since both water molecules are in a trigonal environment, the frequency sequence of the librations should be rock > twist > wag and the intensity sequence should be wag > rock > twist.<sup>45</sup> All librational modes increase in intensity, decrease in half-width and shift to higher frequencies at LNT as compared to ambient temperature. In agreement with these findings, the bands at 768 and 577  $cm^{-1}$  in the IR spectrum at ambient temperature are attributed to rocking and wagging vibrations, respectively (Figure 3a). At LNT, doublet bands at 795, 775, 600 (shoulder) and 572  $cm^{-1}$  are observed for each mode (Figure 3b). In the IR spectrum of 40 % deuterated sample, new bands appear at 507, 490, 427 and 416  $cm^{-1}$  at LNT (Figure 3d). The two lower frequency bands are due to the wagging modes of  $D_2O$  molecules (isotopic ratio 1.34), while the two higher frequency bands are assigned to the twisting vibrations of  $D_2O$ . Using the isotopic ratio 1.41–1.42 found for the twisting vibration<sup>45</sup> in the protonated sample, this mode has to occur in the region of 680–700  $cm^{-1}$ , where the bending vibrations of OCO ions also appear. Probably, the band at 693  $cm^{-1}$  at LNT (688  $cm^{-1}$  at ambient temperature) is due to the twisting mode of  $H_2O$  and/or  $\delta_s(OCO)$  (Table I). On deuteration, the rocking vibration exhibits an isotopic ratio of 1.37–1.39. Using this ratio, the rocking modes of the water molecules have to move to the region of 560–580  $cm^{-1}$ , where the wagging vibrations of the residual  $H_2O$  molecules also appear. Probably, the band at 570  $cm^{-1}$  in the spectrum of the deuterated sample contributes to both rocking vibrations of  $D_2O$  and wagging vibrations of  $H_2O$  molecules, which could explain the broadness of this band in the spectrum of the deuterated sample (Figure 3b and 3d).

*Vibrations due to Hydroxyl Groups of AcOH Molecules.* – As commented above, CAHAC belongs to type B acid carboxylic salts in Speakman's classification. There are significant differences in the OH stretching mode region between the vibrational spectra of the type A and type B salts, which are discussed in the literature.<sup>1–3</sup> The main spectral feature of type A salts is a very strong and broad absorption below 1200  $cm^{-1}$ , assigned to the stretching vibration of the symmetric hydrogen bonds ( $\nu_{OH \cdots O}$ ). Spectra of this type are denoted by Hadži as »(ii) group spectra.«<sup>1</sup> Type B acid salts exhibit the so designated »(i) group« vibrational spectra, which are characterized by the appearance of several, most often three broad bands in the region of 2900–1600  $cm^{-1}$ , known as ABC bands. They have a complicated structure and are made up of a large number of unresolved components. Thus, ABC bands appear near 2900, 2600 and 1900  $cm^{-1}$  in the case of carboxylic dimers and adducts.<sup>1,33–35</sup> With increasing the hydrogen bond strength,



the bands near  $2900\text{ cm}^{-1}$  (A band) and  $2600\text{ cm}^{-1}$  (B band) shift to lower frequencies, whereas the third band (C band) remains practically firm.<sup>1,2,22–24,46</sup> At the same time, the intensities of both A and B bands decrease with decreasing O-H...O bond distances, whereas the C band increases in intensity. Furthermore, the C being strong, the A band vanishes simultaneously in intensity, which makes the  $\bar{\nu}(\text{AB})$  approach the frequency of the B band, *i.e.*, a (AB)  $\leftrightarrow$  C »doublet« is observed in the spectra.<sup>46</sup> The characteristic ABC trio is also observed in hydrogen phosphates, arsenates, sulphates, selenates at about  $2700$ ,  $2200$  and  $1600\text{ cm}^{-1}$ . An explanation for this behavior of the strongly hydrogen bonded system is still to be found. Several mechanisms as »inter- or intrabond« tunnelling of the proton, Fermi resonances between  $\nu(\text{OH})$  stretching vibrations and overtones of the bending modes ( $2\delta_{\text{OH}}$  and  $2\gamma_{\text{OH}}$ ), and strong or inharmonic coupling of the different  $\nu_{(\text{OH}\cdots\text{O})}$  modes are discussed.<sup>46–49</sup>

It is clearly seen from Figure 5a that mainly two broad bands can be distinguished in the range of  $2800$ – $1800\text{ cm}^{-1}$  in the IR spectrum of CAHAC, which are absent in that of CAAC (compare Figures 5a and 5c). The first band, centered near  $2500\text{ cm}^{-1}$ , is very broad (half-width of  $600\text{ cm}^{-1}$ ) and it has some poorly resolved submaxima of lower intensity (about  $2600$ – $2700\text{ cm}^{-1}$ ). The second band, stronger than the first one, appears in the range of  $2200$ – $1850\text{ cm}^{-1}$  (half-width of  $350\text{ cm}^{-1}$ ) and has two well defined maxima at  $1967$  and  $1918\text{ cm}^{-1}$ . At LNT, there is no essential change in the intensities, positions and half-widths of the two broad bands – only some submaxima become better resolved, for example at  $2700$ ,  $2630$  and  $2500\text{ cm}^{-1}$  (Figure 5b). In the Raman spectrum of CAHAC, two very weak bands centered near  $2450$  and  $1950\text{ cm}^{-1}$  are seen (the spectrum is not shown). Taking into account both the vibrational characteristics of these bands and the literature data, the first broad band at  $2500\text{ cm}^{-1}$  could be designated as a complex (AB) band with vanishing A band (the absorption maxima with low intensity at  $2700$  and  $2630\text{ cm}^{-1}$ ) and the second one (at  $1950\text{ cm}^{-1}$ ) as C band. Frequency positions and intensities of the (AB) and C bands provide evidence for the formation of strong hydrogen bonds<sup>38</sup> in CAHAC in agreement with the calculated hydrogen bond energy and the reported O...O distances of  $2.55\text{ \AA}$ . It should be also mentioned that the profile and position of ABC bands in CAHAC highly resemble those found in other type B acid salts such as  $\text{KHPH}$ <sup>22</sup> and  $\text{KHCO}_3$ <sup>50</sup> with similar hydrogen bond lengths.

The behavior of ABC bands on deuteration is widely discussed in the literature.<sup>1–3,22–24,33–35</sup> However, in the present study the low extent of deuteration of the sample does not allow any comment. Moreover, the presence of crystallization waters, whose OD stretching bands fall in the region where (AB) bands appear (see Figure 5g and 5h) complicate the analysis of the spectra.

As far as the possible origin of (AB) and C bands in CAHAC is concerned, we are not able to answer that question based only on our study and hence we leave it open for further studies and discussions. However, taking into account the tentative interpretations given in the literature, we might mention that some overtones ( $2\delta_{\text{OH}}$  ( $\approx 2700\text{ cm}^{-1}$ ),  $2\nu_{\text{C-O}}$  ( $\approx 2600\text{ cm}^{-1}$ ),  $2\gamma_{\text{OH}}$  ( $\approx 2000\text{ cm}^{-1}$ )) and combination vibrations ( $\delta_{\text{OH}} + \gamma_{\text{OH}}$  ( $\approx 2400\text{ cm}^{-1}$ ),  $\nu_{\text{C-O}} + \gamma_{\text{OH}}$  ( $\approx 2400\text{ cm}^{-1}$ )) in the CAHAC spectra have appropriate frequencies to interact with  $\nu_{\text{OH}}$  fundamentals, thus generating (AB)C bands.

#### *Hydrogen Bond Vibrations in $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$*

According to the structural data,<sup>17</sup> the  $\text{H}_2\text{O}(1)$  and  $\text{H}_2\text{O}(2)$  molecules in CAAC (both in  $C_1$  site symmetry) are involved in four different hydrogen bonds. Some structural data are given in Table II. Both  $\text{H}_2\text{O}(1)$  and  $\text{H}_2\text{O}(2)$  are coordinated to Ca(2) ions with similar Ca-O<sub>w</sub> distances.  $\text{H}_2\text{O}(1)$  forms hydrogen bonds with O(6) (non-coordinated acetate oxygen) and O(3) (coordinated to Ca(2)), while  $\text{H}_2\text{O}(2)$  forms hydrogen bonds with O(6) only (O(6) and O(3) belong to the neighboring double-stranded Ca-chains).

The IR spectra of calcium acetate monohydrate in the high frequency region are given in Figure 5c and 5d. A broad band centered at  $3386\text{ cm}^{-1}$  is observed in the spectrum at ambient temperature, while five maxima are clearly seen at LNT (Figure 5d). Bands at  $3462$ ,  $3278$ ,  $3230$  and  $3150\text{ cm}^{-1}$  may be attributed to the OH stretches of water molecules. The corresponding bending vibrations appear at  $1693$  and  $1659\text{ cm}^{-1}$  at LNT (Figure 2f). The maximum at  $3363\text{ cm}^{-1}$  is probably due to the overtone  $2\delta_{\text{H}_2\text{O}}$ . Water librations are better seen in the spectrum at LNT (Figure 3f). Bands at  $768$  and  $750\text{ cm}^{-1}$  (shoulder) are attributed to the rocking modes and those at  $711$  and  $555\text{ cm}^{-1}$  to twisting and wagging vibrations, respectively.

Four uncoupled OD modes are expected to appear in the IR spectrum of the isotopically diluted sample, corresponding to the four hydrogen bond lengths. However, at ambient and liquid nitrogen temperatures the spectra reveal only two bands at  $2354$  and  $2441\text{ cm}^{-1}$  (data at LNT), which show a positive temperature dependence (Figure 5i and 5j). This experimental result cannot be simply explained by the available structural data because: (i) hydrogen bond lengths are too different – from  $2.7$  to  $3\text{ \AA}$  (see Table II) and a large difference in the  $\nu_{\text{OD}}$  modes (about  $150$ – $200\text{ cm}^{-1}$ ) should be expected in accordance with Mikenda's correlation curve.<sup>44</sup> Actually, the frequency separation observed between the two  $\nu_{\text{OD}}$  modes is only  $87\text{ cm}^{-1}$ ; (ii) the proton donor strength of  $\text{H}_2\text{O}(1)$  and  $\text{H}_2\text{O}(2)$  is practically equal (too close Ca-O<sub>w</sub> distances); (iii) three of the hydrogen bonds are formed with one crystallographic type oxygen (O(6)), exhibiting one and the same acceptor ability with respect to water

protons. Taking into account these considerations, the  $\nu_{\text{OD}}$  modes could not be assigned unambiguously, but their frequency positions evidence that the water molecules in calcium acetate monohydrate form intermediate strong hydrogen bonds.<sup>38,45</sup>

## CONCLUSION

Analysis of the IR and Raman spectra of calcium hydrogen triacetate monohydrate,  $\text{CaH}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ , confirms, from the spectroscopic point of view, the structural data that this compound belongs to type B acid salts in Speakman's classification. Thus, the  $\delta_{\text{OH}}$  and  $\gamma_{\text{OH}}$  modes ( $\delta_{\text{OD}}$  and  $\gamma_{\text{OD}}$ , respectively) are found to appear at wavenumbers close to those in other type B acid salts, but they are at lower wavenumbers than those in type A salts. The main spectral feature in the region above 1800  $\text{cm}^{-1}$  is the appearance of two broad bands at about 2500 and 1950  $\text{cm}^{-1}$ , designated as (AB) and C bands, respectively. They are probably due to some overtones and combinations involving OH bending modes enhanced by Fermi resonance with the  $\nu_{\text{OH}}$  fundamentals. The energy of hydrogen bonds ( $-\Delta H$  of formation) formed between the acetic acid moieties is calculated to be 52.7 and 48.4  $\text{kJ mol}^{-1}$ , respectively, using the frequencies of the  $\gamma_{\text{OH}}$  modes. The profile and frequency positions of ABC bands as well as the calculated values of  $\Delta H$  provide evidence for the formation of strong hydrogen bonds<sup>38</sup> in agreement with the reported O...O distances of 2.55 Å. Frequencies of the OH and uncoupled OD modes (isotopically diluted sample) of crystallization water show that the  $\text{H}_2\text{O}(2)$  molecules form stronger hydrogen bonds than the  $\text{H}_2\text{O}(1)$  molecules and that the non-coordinated acetate oxygen is stronger hydrogen bond acceptor than the carbonyl oxygen. The IR and Raman spectra of the neutral salt,  $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , are also presented and discussed. Wavenumbers of the uncoupled OD modes in  $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  reveal that crystallization water forms intermediate strong hydrogen bonds.

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## REFERENCES

1. D. Hadži, *Pure Appl. Chem.* **11** (1965) 435–453.
2. D. Hadži, *Chimia* **26** (1972) 7–13.
3. D. Hadži and B. Orel, *J. Mol. Struct.* **18** (1973) 227–239.
4. B. Orel and D. Hadži, *Spectrochim. Acta, Part A* **32** (1976) 1731–1737.
5. V. Videnova-Adrabińska, J. Baran, and H. Ratajczak, *Spectrochim. Acta, Part A* **42** (1986) 641–648.
6. M. Kemisher, P. Becker, C. Carabatos-Nedelec, F. Brehat, and B. Wyncke, *Ferroelectrics* **124** (1991) 115–119.
7. A. Stöckli, B. H. Meier, R. Kreis, R. Meyer, and R. R. Ernst, *J. Chem. Phys.* **93** (1990) 1502–1520.
8. J. Mavri and J. Grdadolnik, *J. Phys. Chem. A* **105** (2001) 2045–2051.
9. J. Stare and J. Mavri, *Comput. Phys. Commun.* **143** (2002) 222–240.
10. R. E. Newnham, *Structure-Property Relations*, Springer-Verlag, Berlin, 1975.
11. Landolt – Börnstein, *Ferroelectrics and Related Substances*, in: L.-H. Hellwege (Hrsg.), *Group III: Solid State Physics*, Vol. 16, Springer-Verlag, Berlin, New York, Heidelberg, 1982.
12. S. Piana and P. Carloni, *Proteins* **39** (2000) 26–36.
13. P. Baraldi and G. Fabbri, *Spectrochim. Acta, Part A* **37** (1981) 89–92.
14. D. Stoilova, G. St. Nikolov, and Chr. Balarev, *Izv. Khim.* **9** (1976) 371–381.
15. Chr. Balarev, D. Stoilova, and L. Demirev, *Z. Anorg. Allg. Chem.* **410** (1974) 75–87.
16. E. A. Klop and A. L. Spek, *Acta Crystallogr., Sect. C* **40** (1984) 1817–1819.
17. E. A. Klop, A. Schouten, P. van der Sluis, and A. L. Spek, *Acta Crystallogr., Sect. C* **40** (1984) 51–53.
18. J. C. Speakman, *Struct. Bond.* **12** (1972) 141–149.
19. D. Hadži, B. Orel, and A. Novak, *Spectrochim. Acta, Part A* **29** (1973) 1745–1753.
20. V. Videnova-Adrabińska, J. Baran, and H. Ratajczak, *J. Mol. Struct.* **145** (1986) 33–43.
21. D. Hadži, M. Obradovič, B. Orel, and T. Solmajer, *J. Mol. Struct.* **14** (1972) 439–450.
22. B. Orel, D. Hadži, and F. Cabassi, *Spectrochim. Acta, Part A* **31** (1975) 169–182.
23. J. de Villepin and A. Novak, *Spectrochim. Acta, Part A* **27** (1971) 1259–1270.
24. J. de Villepin and A. Novak, *Chem. Phys.* **48** (1980) 113–119.
25. J. L. Delabre and L. Mauty, *Can. J. Appl. Spectrosc.* **37** (1992) 100–105.
26. T. C. Downie, W. Harrison, and E. S. Raper, *Acta Crystallogr., Sect. B* **27** (1971) 706–712.
27. D. E. Irish, J. Semmler, N. J. Taylor, and G. Toogood, *Acta Crystallogr., Sect. C* **47** (1991) 2322–2324.
28. T. Ishioka, Y. Shibata, M. Takahashi, I. Kaneshaka, Y. Kitagawa, and K. Nakamura, *Spectrochim. Acta, Part A* **54** (1998) 1827–1836.
29. M. Haurie and A. Novak, *Spectrochim. Acta* **21** (1965) 1217–1228.
30. A. M. Heyns, *J. Mol. Struct.* **11** (1972) 93–103.
31. V. Koleva and D. Stoilova, *J. Mol. Struct.* **611** (2002) 1–8.
32. F. E. G. Henn, G. M. Cassanas, J. C. Giuntini, and J. V. Zanchetta, *Spectrochim. Acta, Part A* **50** (1994) 841–849.
33. U. Wolfs and H. O. Desseyn, *Spectrochim. Acta, Part A* **51** (1995) 1601–1615.
34. S. E. Odinkov, A. V. Iogansen, and A. K. Dzizenko, *Zh. Prikl. Spektroskopiya* **14** (1971) 418–424.
35. D. Hadži and N. Kobilarov, *J. Chem. Soc. A* (1966) 439–445.
36. G. Cassanas, E. Fabregue, and L. Bardet, *Spectrochim. Acta, Part A* **43** (1987) 735–739.
37. L. Angeloni, M. P. Marzocchi, D. Hadži, B. Orel, and G. Sbrana, *Spectrochim. Acta, Part A* **33** (1977) 735–744.

38. A. Novak, *Struct. Bond.* **18** (1974) 177–216.
39. M. Sh. Rozenberg, *Spectrochim. Acta, Part A* **52** (1996) 1559–1563.
40. H. D. Lutz, J. Henning, W. Buchmeier, and B. Engelen, *J. Raman Spectrosc.* **15** (1984) 336–342.
41. H. D. Lutz, W. Eckers, J. Henning, M. Jung, and W. Buchmeier, *Thermochim. Acta* **74** (1984) 323–330.
42. I. Savatinova and E. Anachkova, *Phys. status solidi B* **91** (1979) 413–419.
43. M. A. White and M. Falk, *J. Chem. Phys.* **84** (1986) 3484–3490.
44. W. Mikenda, *J. Mol. Struct.* **147** (1986) 1–15.
45. H. D. Lutz, *Struct. Bond.* **69** (1988) 97–125.
46. S. E. Odinokov and A. V. Iogansen, *Spectrochim. Acta, Part A* **28** (1972) 2343–2350.
47. C. A. Cody and R. Khanna, *Indian J. Pure Appl. Phys.* **16** (1978) 296–303.
48. H. Ratajczak, A. Yaremko, and J. Baran, *J. Mol. Struct.* **275** (1992) 235–247.
49. H. Abramczyk, *Vib. Spectrosc.* **5** (1993) 109–117.
50. G. Lucazeau and A. Novak, *J. Raman Spectrosc.* **1** (1973) 573–586.

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## SAŽETAK

### Vibracijsko ponašanje kalcijeva vodikova triacetata monohidrata, $\text{CaH}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$

Violeta Koleva

Infracrveni (IR) i Ramanovi spektri kalcijeva vodikova triacetata monohidrata,  $\text{CaH}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ , (po Speakmanovoj klasifikaciji: kisela sol tipa B), prikazani su u frekvencijskome području  $4000\text{--}400\text{ cm}^{-1}$ . Razmatrani su s obzirom na osnovne vibracije specija octene kiseline ( $\text{CH}_3\text{COO}^-$  i  $\text{CH}_3\text{COOH}$ ) i vibracije vodikovih veza hidroksilnih skupina iz  $\text{CH}_3\text{COOH}$  te molekula vode. Glavno spektralno obilježje u području istezanja  $\nu(\text{OH})$  jest pojava dviju širokih vrpca pri približno  $2500$  i  $1950\text{ cm}^{-1}$ , označenih kao vrpce (AB) odnosno C. Nazočnost vrpca ABC s položajem pripadnih frekvencija i intenziteta, te frekvencija  $\delta_{\text{OH}}$  i  $\gamma_{\text{OH}}$ , spektroskopski je dokaz za postojanje jakih asimetričnih vodikovih veza među specijama octene kiseline. Izračunane su entalpije njihova stvaranja ( $\Delta H$ ) i dobivene su vrijednosti  $-48,4$  i  $-52,7\text{ kJ mol}^{-1}$ . Frekvencije raspregnutih OD istezanja kristalne vode pokazuju, da  $\text{H}_2\text{O}$  (2) tvori jače vodikove veze nego  $\text{H}_2\text{O}$ (1) te da je nekoordinirani acetatni kisik jači akceptor vodikove veze od karbonilnoga kisika. Također su prikazani i prodiskutirani IR i Ramanovi spektri  $\text{CaH}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ .