Raman Spectroscopic Studies on Aqueous Sodium Formate Solutions and DFT Calculations

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Abstract
NaHCOO(aq) and NaDCOO(aq) solutions were measured using Raman spectroscopy from dilute to concentrated solutions at 23 °C in water and heavy water from 50 to 4300 cm⁻¹. A concentrated NaHCOO solution in heavy water was also measured. The Raman band parameters of HCOO⁻(aq) and DCOO⁻(aq) such as peak position, full width at half maximum (fwhm), integrated intensities, and depolarization values were determined. From the Raman spectroscopic data, it was concluded that the HCOO⁻(aq) and DCOO⁻(aq) symmetry is lower than C₂ᵥ and probably as low as C₁. In contrast to the solution state, HCO⁻(DCO⁻) possess C₂ᵥ symmetry in the gas phase and the DFT frequencies are given. DFT frequencies on a cluster of HCOO⁻/DCOO⁻ with five implicit water molecules in the first sphere and placed in a polarizable continuum deviate not more than 1–2% from the measured ones. In the Raman spectrum in NaHCOO(aq), a band doublet at 2730 cm⁻¹ and 2820 cm⁻¹ occurs instead of a single band. The band doublet is due to Fermi resonance and results from the interaction of the overtone of the bending C–H mode, 2ν₆ at 1382 cm⁻¹ and ν₁. The undisturbed C–H stretching mode, ν₁ amounts to 2785 cm⁻¹. In DCOO⁻(aq), a Fermi doublet was also observed at 2030.5 and 2116.5 cm⁻¹, and the undisturbed wave-number position amounts to 2101 cm⁻¹. Furthermore, a solution of HCOO⁻ in D₂O showed slightly changed frequencies compared with the ones in water caused by the solvent isotope effect. Ion pairing between Na⁺ and HCOO⁻ characterizes the Raman spectrum at high solute concentrations which are melt-like enabling direct contact between the ions. A NaHCOO solution with high amounts of LiCl added showed showed large perturbations of the HCOO⁻ bands especially ν₅COO⁻ and δ COO⁻ of HCOO⁻and revealed a stronger affinity of Li⁺ toward HCOO⁻. The ion pairs formed are most likely contact ion pairs between Li⁺ and HCOO⁻ which have different stoichiometry of Li⁺: HCOO⁻ such as 1:1 and 2:1.
**Graphical Abstract**

NaHCOO(aq) and NaDCOO(aq) solutions were measured using Raman spectroscopy from dilute to concentrated solutions at 23 °C and the band parameters of HCOO−(aq) and DCOO−(aq) are given. DFT frequencies on HCOO−-water cluster were calculated and compared with those measured. Ion pairs in concentrated aqueous solutions of NaHCOO and NaHCOO/LiCl were characterized. Shown are the Raman spectra of NaDCOO(aq) (top) and NaHCOO(aq) (bottom).

**Keywords** Raman spectroscopy · NaHCOO and NaDCOO solutions · Vibrational normal modes · Terahertz wavenumber region · DFT structures and frequency calculations · PCM calculations

**1 Introduction**

Formate and its corresponding acid, formic acid, is used commercially in various fields, such as in industry, grass silage as a preservative, and antibacterial agent in livestock feed, leather tanning, anti-icing, textile dyeing, finishing, food additives, natural rubber, drilling fluids, and various chemical processes [1]. Formate is the simplest carboxylate anion and its solution structure has been studied by theoretical and structural methods in recent years [2–6]. Dielectric Resonance spectroscopy (DRS) was employed on aqueous solutions of sodium formate and acetate. The study revealed extensive hydration of formate in aqueous solution as slow water at DRS time scale [7]. Ab initio and molecular dynamics studies have been carried out on the hydration of HCOO− reporting the solution geometry and a hydration number at ~5 [2, 3]. Despite the simplicity of the formate ion, the symmetry of the hydrated formate, HCOO−(aq), is uncertain to this day. Although Raman and infrared studies have been published on HCOO−(aq), the deduced symmetry was either C2v or Cs [8, 9]. It will be shown that neither symmetry assignments can be correct in aqueous solution state. The symmetry C2v is unlikely because the vibrational modes of the carboxylate group, –COO−, are polarized and this is not in accordance with symmetry C2v. The symmetry Cs is also unlikely because not only are the symmetry elements C2 and σV lost due to unsymmetric hydration in aqueous solution but the symmetry plane σV′ is also lost.

In this study, we report and discuss the Raman spectra of NaHCOO and NaDCOO in water over a large concentration range. A solution of NaHCOO was prepared in heavy water as well. The Raman spectra were measured in dilute and concentrated solutions and from 50 to 4300 cm−1. The symmetry of the carboxylate ion was deduced from the data of the Raman bands. Band parameters of the vibrational modes were determined such as peak positions, band width, depolarization degree of the modes, and band intensities of
the hydrated ion. Special care has been devoted to precise measurement of depolarization properties of the bands because from these values the symmetry state of the hydrated anion follows.

Raman spectroscopy has the advantage that the Raman signal is directly proportional to the species concentration. Raman spectra in the wavenumber range from 50 to 4300 cm\(^{-1}\) were recorded. In the terahertz region and low wavenumber region, a R-normalization correction is necessary. A small slit width employed in this study guarantees the measurement of correct band profiles. Furthermore, Raman scattering offers the construction of isotropic scattering from the parallel and perpendicular profiles. The depolarization degree of the bands is also a valuable quantity characterizing the modes. Finally, the isotropic scattering profile can be calculated which reflects the true vibrational contribution. (See discussion under Experimental Section for further details below and Ref. [10]).

In conjunction with the spectroscopic data on the formate, density functional theory (DFT) B3LYP calculations have been carried out using the basis set 6-311++(3df,2pd). Calculations have been performed on the bare HCOO\(^{-}\) and DCOO\(^{-}\) and also by placing both formate ions in a polarizable continuum (PC) solvation sphere applying the PC model (PCM) thereby, simulating the hydration effect. In order to account for the directional nature of the H-bonds formed in aqueous solution, calculations have been carried out on several formate–water clusters, HCOO\(^{-}\)\(\cdot\)\(n\)H\(_2\)O \((n = 1–5)\) with \(n\), the number of the water molecules in the first sphere. The cluster with five water molecules in the first sphere was placed in a polarizable continuum. A cluster with five water molecules in the first sphere and a sixth in the second sphere was also considered. Geometrical parameters such as bond length, bond angles, and dihedral angle were obtained. The unscaled vibrational frequencies and depolarization values of the modes from the DFT calculations were then compared with the experimental spectra. The geometry of a HCOO\(^{-}\) cluster with 4 water molecules and Na\(^{+}\) as well as Li\(^{+}\) was also optimized and the frequencies and depolarization values were calculated.

2 Experimental Section and DFT Calculations

2.1 Solution Preparation

Sodium formate was purchased from Fluka (now Merck, Darmstadt, 99.5%) and was dried over a molecular sieve. The salt solutions were prepared by weight with triply distilled water in 50-mL glass flasks. The solution densities were measured at 23 °C with a pycnometer, as previously reported, and concentrations in mole per kilogram were calculated [11]. The following solutions were prepared at 23 °C (standard uncertainty \(= 6 \times 10^{-5}\)):

- \(9.245 \text{ mol·L}^{-1} (13.293 \text{ mol·kg}^{-1})\),
- \(7.888 \text{ mol·L}^{-1} (10.622 \text{ mol·kg}^{-1})\),
- \(6.123 \text{ mol·L}^{-1} (7.595 \text{ mol·kg}^{-1})\),
- \(4.878 \text{ mol·L}^{-1} (5.737 \text{ mol·kg}^{-1})\),
- \(3.980 \text{ mol·L}^{-1} (4.519 \text{ mol·kg}^{-1})\),
- \(2.008 \text{ mol·L}^{-1} (2.132 \text{ mol·kg}^{-1})\),
- \(1.001 \text{ mol·L}^{-1} (1.0305 \text{ mol·kg}^{-1})\),
- \(0.732 \text{ mol·L}^{-1} (0.7486 \text{ mol·kg}^{-1})\),
- \(0.312 \text{ mol·L}^{-1} (0.3154 \text{ mol·kg}^{-1})\),
- \(0.102 \text{ mol·L}^{-1} (0.1025 \text{ mol·kg}^{-1})\),

and \(0.0645 \text{ mol·L}^{-1} (0.06477 \text{ mol·kg}^{-1})\). A very concentrated solution at 13.747 mol·kg\(^{-1}\) (9.459 mol·L\(^{-1}\)) was prepared by mixing an excess of salt into distilled water. The temperature was kept constant at (23 ± 0.1) °C over a period of 20 days and the solution was then separated from the solid.
A NaHCO$_3$ solution in heavy water at 9.020 mol·L$^{-1}$ was prepared from the dried anhydrous salt with heavy water from Merck, Darmstadt (99.85% D).

Three solutions of NaDCO$_2$ (Sigma-Aldrich, now Merck, Darmstadt, 99.5 atom % D) in water were prepared by weight with a concentration at 3.950 mol·L$^{-1}$, 1.9725 mol·L$^{-1}$, and 0.861 mol·L$^{-1}$. Further dilution resulted in solutions at 0.287 mol·L$^{-1}$, 0.1435 mol·L$^{-1}$, and 0.0718 mol·L$^{-1}$.

Furthermore, two solutions were prepared containing 0.732 mol·L$^{-1}$ NaHCO$_3$ with an addition of 4.028 mol·L$^{-1}$ and 8.140 mol·L$^{-1}$ LiCl. The molar concentrations were 4.107 mol LiCl and 0.750 mol NaHCOO pro 1000 g H$_2$O (mole ration Li$^+$: HCOO$^-$ = 5.47) for the first solution and for the latter 8.297 mol LiCl and 0.750 mol NaHCOO pro 1000 g H$_2$O (mole ration Li$^+$: HCOO$^-$ = 11.06).

### 2.2 Spectroscopic Measurements

Raman spectra were measured in the macro chamber of the T 64000 Raman spectrometer from Jobin Yvon in a 90° scattering geometry at 23 °C and the measurements described in detail elsewhere [12, 13]. The spectra were excited with the 514.532 nm line of an Ar$^+$ laser at a power level of 1500 mW at the sample. The NaDCOO(aq) solutions, however, were measured with a much smaller laser power at 180 mW. After passing the spectrometer in subtractive mode, with gratings of 1800 grooves/mm, the scattered light was detected with a cooled CCD detector. The $I_{VV}$ (polarized) and $I_{VH}$ (depolarized or anisotropic) scattering spectra were obtained with fixed polarization of the laser beam by rotating the polarizer at 90° between the sample and the entrance slit. The following scattering geometries are defined as

$$I_{VV} = I(Y[ZZ]X) = 45\alpha'^2 + 4\gamma'^2$$  \hspace{1cm} (1)

$$I_{VH} = I(Y[ZY]X) = 3\gamma'^2$$  \hspace{1cm} (2)

From the two scattering geometries (1) and (2), the isotropic spectrum, $I_{iso}$ is constructed:

$$I_{iso} = I_{VV} - \frac{4}{3}I_{VH}$$  \hspace{1cm} (3)

The depolarization ratio, $\rho$, of the Raman bands is determined according to Eq. 4:

$$\rho = \frac{I_{VH}}{I_{VV}} = \frac{3\gamma'^2}{(45\alpha'^2 + 4\gamma'^2)}$$  \hspace{1cm} (4)

It should be mentioned that the isotropic (Eq. 3) and anisotropic scattering (Eq. 2) are of true importance from the Raman measurements, while the former contains the vibrational contribution and the latter, vibration and orientation. The depolarized spectrum (Eq. 2) is equivalent to the anisotropic spectrum, and therefore, the terms are used interchangeably.

The polarization analyser was calibrated with CCl$_4$ before each measuring cycle and adjusted if necessary. The depolarisation ratio of the $\nu_1$ mode of CCl$_4$ at 459 cm$^{-1}$ was measured 12 times, and a depolarization ratio at 0.0036±0.0005 was determined. The depolarization ratios of the CCl$_4$ modes at 217 cm$^{-1}$ and 315 cm$^{-1}$ which are depolarized have been determined to 0.75±0.02. Accordingly, these ratios were calculated from
the integrated bands of the polarized and depolarized components. The values are slightly different considering differential depolarization ratios which are calculated from the band heights at band maximum for both components.

A neon lamp was used to calibrate the spectrometer, and the wavenumber accuracy in the subtractive mode of the Raman spectrometer was ±0.4 cm⁻¹. The relatively narrow ν₂ COO⁻ band was determined in the additive mode of the spectrometer with an accuracy of ±0.1 cm⁻¹.

High-resolution measurements of the ν₂ COO⁻ mode at 1350 cm⁻¹ have been achieved applying the triple additive configuration of the spectrometer and, so, it was possible to accurately determine the half width and peak position of the symmetric stretch COO⁻. A resolution equal to 1.1 cm⁻¹ at 1300 cm⁻¹ was achieved using the 514.532 nm Ar⁺ excitation line. This measuring modus allowed the analysis of the true band shape of the symmetric stretch of the COO⁻ moiety.

In order to obtain spectra defined as $R(\tilde{\nu})$ which are independent of the excitation wavenumber $\nu_L$, the measured Stokes intensity should be corrected for the scattering factor $(\tilde{\nu}_L - \tilde{\nu})^3$ in the case of counting methods used. The spectra were further corrected for the Bose–Einstein temperature factor, $B = [1 - \exp(-\hbar \tilde{\nu} c/kT)]$ and the frequency factor, $\tilde{\nu}$, to give the reduced spectrum:

$$R(\tilde{\nu}) = I(\tilde{\nu}) \cdot (\tilde{\nu}_L - \tilde{\nu})^3 \cdot \tilde{\nu} \cdot B$$

(5)

Using the $R_{VV}$ and $R_{VH}$ spectra, the isotropic spectrum in R-format was calculated according to

$$R(\tilde{\nu})_{iso} = R(\tilde{\nu})_{VV} - \frac{4}{3} \times R(\tilde{\nu})_{VH}$$

(6)

In the low wavenumber region, the $I(\tilde{\nu})$ and $R(\tilde{\nu})$ spectra are significantly different and only the spectra in R-format are presented. It should be noted that one of the advantages of using isotropic R-spectra is that the baseline is almost flat in the 45–700 cm⁻¹ wavenumber region allowing relatively unperturbed observation of any weak modes present free of the Rayleigh wing [10].

### 2.3 DFT Calculations

The DFT calculations were carried out with Gaussian 16 (Ref. [14]) employing Becke’s three-parameter hybrid exchange functional coupled with the Lee–Yang–Parr correlation functional (B3LYP) at the 6-311++G(3df,2pd) level of theory. Reasonable descriptions of anions with electrons located on average relatively far from the nuclei require polarization basis sets and diffuse orbitals. In all cases, the geometry was optimized to obtain a local minimum on the potential energy surface (PES) without imaginary vibrational frequencies. In a first approach, the hydration of the formate ion was modeled by placing the anion in an isotropic and homogeneous continuum characterized by the dielectric property for water at 78.3. The polarizable continuum model (PCM) implemented in the Gaussian package was used (see for more details Ref. [15]) in order to take the hydration effect into account. In a second approach, the explicit hydration approach, the following discrete cluster structures were considered: in addition to the bare HCOO⁻, HCOO⁻·H₂O, NO₃⁻·2H₂O, HCOO⁻·4H₂O, HCOO⁻·5H₂O and HCOO⁻·5H₂O·H₂O. The H-bonding of the water molecules around the –CO₂ group has been investigated, and bond lengths, bond angles, and dihedral angle were determined reflecting the influence on the formate ion.
The cluster with explicit hydration, $\text{HCOO}^-\cdot5\text{H}_2\text{O}$, was also optimized applying a polarizable continuum model.\(^1\) Vibrational frequencies and depolarization ratios were calculated for all models thereby using unscaled frequencies throughout. The interpretation of the spectroscopic results for the concentrated solutions was accompanied by calculations on $\text{Na}^+(\text{OH}_2)_4\text{HCOO}^-$ and $\text{Li}^+(\text{OH}_2)_4\text{HCOO}^-$ clusters. Furthermore, sodium(I)–water clusters, $\text{Na}^+(\text{OH}_2)_n$ with $n=4$ and 5 water molecules were calculated in a recent work \([11]\) applying the DFT method at the same level of theory and the results represent a local minimum structure.

3 Experimental Results and Discussion

The paper is organized as follows: first, the structures and symmetry of formate in the gas phase were calculated under the harmonic as well as the anharmonic approximation. These results were discussed in light of the infrared results of $\text{HCO}_2^-$ in a neon matrix. However, the vibrational frequency calculation of formate in aqueous solution is more complicated, and the hydration effect has to be taken into account. The simplest approach would be the calculation of the formate ion in a polarizable continuum, applying the PC model or calculating the formate ion in discrete water clusters. Both approaches were applied. Discrete cluster calculations on $\text{HCOO}^-\cdot\text{nH}_2\text{O}$ with $n=1–5$ water molecules were considered in order to show an evolution of the number of water molecules on the formate structure and frequencies. The cluster with 5 water molecules represented the most realistic model. This discrete cluster with its 5 water molecules in the first sphere was also placed into a polarizable continuum (PCM) in order to approximate the bulk water. Finally, a cluster with 5 water molecules in the first sphere and a sixth in the second sphere ($\text{HCOO}^-\cdot5\text{H}_2\text{O}\cdot\text{H}_2\text{O}$) was studied. A discussion and assignment of the Raman spectroscopic intramolecular formate bands of $\text{HCOO}^-$ and $\text{DCOO}^-$ in aqueous solutions then follows. Spectra of a concentrated solution of $\text{HCOO}^-$(aq) and $\text{HCOO}^-(\text{D}_2\text{O})$ were presented and discussed, showing the influence of water and heavy water on the modes of formate. The DFT frequencies of a discrete $\text{HCOO}^-$ cluster with 5 water molecules with solvation (PCM) are discussed in conjunction with these Raman spectroscopic results to support the assignments. Then, a brief discussion of the terahertz wavenumber region is given, including the spectral influence of the $\text{Na}^+(\text{aq})$ and the restricted translation modes of formate and water. Furthermore, the band doublet of $\nu_1$, the C–H stretching mode is shown to be due to Fermi resonance of the overtone of $2\nu_6$, the C–H in-plane deformation mode and $\nu_1$. The influence of the NaHCOO on the O–H stretching band of water, a broad band with two maxima at 3245 and 3496 cm\(^{-1}\), is briefly touched upon. Finally, results are given and discussed on ion-pair formation of formate with Na\(^+\) and Li\(^+\) at the concentrated solution stage.

\(^1\) We are aware that our cluster models include only a small number of water molecules in the first hydration sphere of formate. \([16]\). However, for vibrational analysis in Ref. \([16]\), in the end, only clusters with five to six water molecules were taken into account. Furthermore, the presented ATR infrared spectral data in Ref. \([16]\) for the two $\text{–COO}^-$ stretching modes have been used as a benchmark for their simulation results. The ATR bands, however, have to be corrected with respect to $d_p$ and polarization of the infrared radiation etc. The usage of such ATR spectra” should not be a sophisticated one”; in other words, exact peak positions and band shapes are questionable (see Ref. \([17]\) (Chpt. 4.5. Attenuated Total Reflection for detailed ATR FTIR analysis). Furthermore, a statement by Habka et al. \([16]\) to favor ATR FTIR for band shape analysis rather than Raman spectroscopy has to be viewed with caution.
### 3.1 Structure, Symmetry, and Vibrational Modes of HCOO⁻: Gas Phase, Neon Matrix, and Aqueous Solution

First, we start with the structure and the symmetry of HCOO⁻ (and DCOO⁻) in the gas phase. The symmetry of this planar molecule ion is C₂v and DFT calculations on bare HCOO⁻ ion result in a structure with all four atoms lying in the symmetry plane, σᵥ. The molecule also possesses a rotational axis C₂ and a symmetry plane σᵥ thereby defining the gas phase symmetry of HCOO⁻ in vacuo as C₂v. The HCOO⁻ structure is given in Fig. 1 at the left side and at the right side is the formate cluster with 5 explicit water molecules which will be discussed further below. Table 1 summarizes the geometrical data for the HCOO⁻ gas phase structure as well as the one for cluster models HCOO⁻·5H₂O which will be discussed.

For HCOO⁻ in vacuo, it follows that the planar molecule ion demands a dihedral angle (∠ OCOH) at 180°. The dipole moment of the HCOO⁻ amounts to 1.389 Debye. Both of the C–O bonds in this structure are equivalent. The formate ion in the gas phase has the following structure parameters: bond length C–O at 1.249 Å and C–H at 1.136 Å, COO bond angle at 130.44° and the dihedral angle at 180°.

In aqueous solution, however, formate is hydrated, and the absolute standard molar enthalpy is −432 kJ·mol⁻¹ at 25 °C. (Standard molar enthalpy for HCOO⁻ is only ~18% lower than for instance F⁻ which amounts to ΔHf = −510 kJ·mol⁻¹ at 25 °C [18]). Calculated DFT enthalpies of the stepwise hydration reaction of the formate ion in the gas phase from n = 1 to 5 H₂O molecules are summarized in Table 6. These enthalpy data allowed us to compare our DFT data with available experimental data (n = 1–3) which were measured by the thermal detection-mass spectrometry [19, 20].

The strong hydration of formate in solution has also been deduced from DR spectroscopy and a hydration number equal to 5.2 at infinite dilution was obtained. The dynamics of the hydrated water was evidenced by observing a few water molecules...
irrotationally bound (frozen) but mostly as slow water [7]. Furthermore, computer simulations of carboxylate hydration [2, 21, 22] concluded that water is highly structured around the –COO− group, with an average hydration number of 5–7. NMR studies have suggested that there are 5.0–6.5 water molecules around each –COO− group [23].

The environmental effect caused by hydration in aqueous solution on formate will influence the force field of the normal modes and its symmetry. The symmetry of the formate ion in its hydration cage might be lowered compared to the one in the gas phase. The dynamics of the hydrated water was evidenced by observing the hydration water as slow water on the timescale of DR [7] which is of several picoseconds. The period T of a vibration at 1500 cm−1, however, is 20 fs and is therefore short enough to record a few thousand vibrations in such a hydration environment. In fact, the lowering of the symmetry of anions other than formate in aqueous solution has been observed in studies on NO−3 (aq) [11] and CO2−3 (aq) [13]. The strong influence on the formate in the unsymmetric environment of liquid water leads to a lower symmetry, and in case of C1 symmetry, all Raman modes would be partially polarized. It should be mentioned that the observed Raman depolarization values for the HCOO− bands dictate that the molecular ion must be surrounded by an unsymmetrical environment. To show that such an unsymmetric hydration environment exists in solution, we performed DFT calculations on HCOO− clusters with explicit hydration with 1 to 6 water molecules. The hydration effect in aqueous solution may also be modeled applying the polarizable continuum method (PCM) in contrast to the discrete cluster model with implicit water molecules. The PCM gives quite realistic vibrational frequencies for HCOO−(aq) but it is unable to account for the directionality of the H-bonds between formate and H2O [24], and the symmetry of formate remains C2v. A slight distortion of formate evidenced by the dihedral angle of the ion smaller than 180° in clusters with an implicit water sphere leads to symmetry C1.

### Table 1

| Geometrical parameters such as bond lengths aij (in Å), angles aijk and dihedral angle, α2,1,3,4 (see Fig. 2) for HCOO− in vacuo, HCOO− plus PCM, cluster HCOO−(H2O)5 and the same cluster plus PCM derived from DFT calculations using B3LYP/6311++G(3df,2pfd) |
|-----------------------------------------------|
| HCOO− in vacuo | HCOO− + solvation sphere | HCOO−(H2O)5 | HCOO−(H2O)5 + solvation sphere |
| a1,2 | 1.249 | 1.252 | 1.249 | 1.250 |
| a1,3 | 1.249 | 1.252 | 1.259 | 1.262 |
| a1,4 | 1.136 | 1.118 | 1.109 | 1.105 |
| α2,1,3,4 | 130.44° | 128.31° | 127.08° | 126.34° |
| a2,6 | 1.833 | 1.837 |
| a2,15 | 1.794 | 1.773 |
| a3,9 | 2.127 | 2.057 |
| a3,12 | 1.945 | 1.823 |
| a3,18 | 1.798 | 1.779 |
| a2,5 | 2.809 | 2.809 |
| a2,14 | 2.774 | 2.755 |
| a3,8 | 3.036 | 2.985 |
| a3,11 | 2.886 | 2.800 |
| a3,17 | 2.778 | 2.760 |
A realistic cluster with five water molecules, HCOO⁻·5H₂O forming five fairly strong H-bonds, is shown in Fig. 1 (right side). In Table 1, the results are given for structural parameters in addition to the bare ion and also the formate ion with solvation (PCM), the HCOO⁻ cluster with five water molecules, and the same cluster with an additional polarizable continuum. The latter model gives realistic structural parameters compared with the ones determined by neutron scattering and X-ray diffraction [6]. Our DFT data on HCOO⁻ are reasonably close to the measured ones, except for the C–H/D bond distance. (See also data in Table E-8 of Supplemental Material, Ref. [25])

The geometrical data from our DFT simulations on formate water clusters with increasing numbers of water molecules in the first hydration sphere from 1 to 5 water molecules on its structure of HCOO⁻ are presented in Table S1. Included is also the bare ion. In addition to these data, the DFT results on a cluster with 5 water molecules in the first sphere, and one in the second sphere is also included in this Table. The DFT frequencies show that the most realistic hydration model for vibrational analysis is the one with 5 water molecules. In addition to the DFT data in Table S1, the structure models are presented in Fig. S1. The structure of the bare HCOO⁻ ion possesses C₂ᵥ symmetry as shown above as does the HCOO⁻·H₂O cluster (structure A, Fig. S1) with a symmetrical bound water molecule. For both structures, the bare ion and structure A, in which the water molecule acts as a double donor, the C–O bonds are equivalent. All the other HCOO⁻·nH₂O clusters with n ≥ 2 and (structures B to E, Fig. S1) lead to an asymmetric environment and therefore to symmetry C₁ for HCOO⁻. Importantly, the planarity of the HCOO⁻ ion is lost in the clusters with n ≥ 2 even if the effect is only slight (Table S1). Furthermore, both C–O bonds are no longer equivalent having slightly different bond lengths. The formate cluster with 6 water molecules hydrating the HCOO⁻ shows five water molecules in the first sphere and the sixth water molecule in the second sphere.

In summary, the results on discrete clusters of HCOO⁻ with 2–5 water molecules, HCOO⁻·nH₂O (n = 1–5), and the cluster HCOO⁻·5H₂O·H₂O demonstrate that the symmetry of the formate might be reduced to C₁ in aqueous solution. The two C–O bonds in this structure are no longer equivalent having two slightly different C–O bonds and HCOO⁻ loses its planar structure. The most realistic model is the HCOO⁻ cluster with 5 water molecules in the first sphere and a polarizable continuum. It should be noted that asymmetric hydration observed for the formate is not uncommon in aqueous solution and has also been observed in NO₂⁻ (aq) and CH₃COO⁻(aq) [11, 24, 26].

3.2 Discussion of the Vibrational Modes in NaHCOO(aq) and NaDCOO(aq)

The irreducible representation for the 6 normal modes of HCOO⁻ is \( \Gamma'_v(C_{2v}) = 3a_1 + 2b_1 + b_2 \), and of the six modes, three are polarized and three depolarized. Also, six infrared modes are expected. The infrared spectrum of HCO₂⁻ in a neon matrix has been published by Forney et al. [25], and the molecule ion possesses C₂ᵥ symmetry as well as the one in the gas phase. The frequencies of the HCO₂⁻ ion in the neon matrix are presented in Table 2 together with our DFT frequencies for the harmonic and anharmonic case. It is noteworthy that the C–H stretching mode appears as a single, weak infrared band, and no Fermi resonance has been observed between \( 2\nu_6 \) and \( \nu_1 \). The comparison of the harmonic and anharmonic DFT frequencies confirms the large degree of anharmonicity for the C–H stretching mode, \( \nu_1 \) (see also [25]). For the deuterated analog, DCO₂⁻ in vacuo, our DFT frequencies in the harmonic and anharmonic approximation are given in Table S2 and compared to
the normal vibrations of DCO$_2^-$ in a neon matrix [25]. As for the $\nu_1$ C–H stretch, the C–D stretch is quite an anharmonic vibration.

The vibrational spectra of the formate in aqueous solution cannot be compared directly with the one in the gas phase or in the neon matrix. The C$_2v$ symmetry for HCOO$^-$ in water is unlikely because the vibrational modes of the carboxylate group, $\nu_2$ and $\nu_5$, were observed as polarized. This is not in accordance with symmetry C$_2v$. For symmetry C$_s$, the irreducible representation of the normal modes would be $\Gamma_v(C_s) = 5a' + a''$ with five polarized modes and one depolarized mode in the Raman effect but is also unlikely in the case for a dihedral angle (\angle OCOH) smaller than 180°. For C$_1$ symmetry, all Raman modes are partially polarized.

The Raman spectroscopic data of the vibrational bands of HCOO$^-$(aq) and DCOO$^-$(aq) are given in Table 3, and an overview spectrum of NaHCOO(aq) is presented in Fig. 2A/B. In addition to the intramolecular modes of HCOO$^-$(aq), the wavenumber range of the O–H water bands is shown. In Fig. 3, the Raman scattering profiles are shown for NaDCOO(aq). In Table S3, the Raman data are given for a concentrated NaHCOO solution in water and heavy water. These results show that the change from water to heavy water influences the HCOO$^-$ vibrational modes slightly due to the isotope effect caused by the solvent.

The broad stretching region of water influenced by the solute, NaHCOO is presented in Fig. S2 and S3. From our Raman spectroscopic data on the water O–H stretching region in NaHCOO(aq) solution, a hydration number was deduced at ~4–5, and a concentration plot of isotropic Raman scattering profiles is presented in Fig. S2 for the O–H stretching band region of H$_2$O for several sodium formate solutions. Polarized and depolarized scattering profiles in the O–H stretching region as well as the depolarization degree over the whole O–H stretching profile are shown in Fig. S3 for a NaHCOO(aq) solution at 9.459 mol·L$^{-1}$ and in comparison, neat water.

Table 2 Vibrational frequencies of HCO$_2^-$ in a solid neon matrix [25] and DFT calculations of harmonic and anharmonic frequencies

| Modes | Description of normal modes | HCO$_2^-$ [25] (Ne-matrix) | Harmonic frequencies | Anharmonic frequencies |
|-------|-----------------------------|-----------------------------|---------------------|-----------------------|
| $\nu_3$ (a$_1$) | OCO scissor | 744.1 | 746.9 | 741.4 |
| $\nu_4$ (b$_1$) | C–H out-of-plane def | – | 1045.7 | 1023.8 |
| $\nu_2$ (a$_1$) | C–O sym. stretch | 1323.0 | 1342.5 | 1316.2 |
| $\nu_6$ (b$_2$) | C–H in-plane def | – | 1374.1 | 1337.5 |
| $\nu_5$ (b$_2$) | C–O antisym. stretch | 1628.9 | 1660.4 | 1631.1 |
| $\nu_1$ (a$_1$) | C–H stretch | 2455.7 | 2567.4 | 2387.7 |

A representation of the normal modes of the HCOO$^-$ with a solvation sphere (PCM) is given in Fig. 4. In addition to the measured frequencies and depolarization values of HCOO$^-$(aq), the DFT frequencies and depolarization values are summarized for the bare HCOO$^-$ in vacuo and those with solvation (PCM) in Table 4. In addition, the frequencies and depolarization values of the discrete cluster model HCOO$^-$·5H$_2$O and the ones of the same cluster in a polarizable continuum (PCM) are presented in this Table. The calculated unscaled frequencies of the HCOO$^-$·5H$_2$O cluster compare favorably with the measured ones within 1–2% accuracy, while the same cluster with a polarizable solvation sphere (PCM) gives even slightly better results. The depolarization values also reflect the measured ones fairly well. A similar comparison of the measured frequencies and depolarization values of DCOO$^-$(aq) with our DFT frequencies for DCO$_2^-$, and the cluster with 5 water
Table 3  Assignments of the Raman bands of HCOO\textsuperscript{−}(aq) and DCOO\textsuperscript{−}(aq) in dilute NaHCOO(aq) and NaDCOO(aq), resp

| Mode  | Normal vibration                    | HCOO\textsuperscript{−}                     | DCOO\textsuperscript{−}                      |
|-------|-------------------------------------|---------------------------------------------|---------------------------------------------|
|       | Band Position | Relative Intensity | FWHM | \(\rho\) | Peak Position | Relative Intensity | FWHM | \(\rho\) |
| \(\nu_3\) | OCO scissor mode               | 762 | 3.84 | 24.0 | 0.33 | 755 | 1.45 | 26.0 | 0.42 |
| \(\nu_4\) | C–H/D out-of-plane deformation | 1066 | 2.66 | 11.4 | 0.73 | 912 | 0.25 | 11.1 | 0.72 |
| \(\nu_5\) | C–O sym. stretch               | 1350 | 100.0 | 13.1 | 0.13 | 1323.8 | 100 | 8.65 | 0.08 |
| \(\nu_6\) | C–H/D in-plane deformation      | 1382 | 6.86 | 20.0 | 0.42 | 1022 | 3.47 | 16.0 | 0.62 |
| \(\nu_5\) | C–O antisym. stretch            | 1585 | 2.13 | 43 | 0.62 | 1580 | 3.00 | 50.1 | 0.64 |
| \(\nu_1\) | C–H/D stretch\textsuperscript{A}  | 2731 | 27.90 | 42.1 | 0.26 | 2030 | 11.60 | 27.5 | 0.33 |
|       |                                    | 2818 | 67.32 | 42.0 | 0.21 | 2116.5 | 52.94 | 29.4 | 0.30 |

The Raman band parameters such as band position, FWHM (both in cm\textsuperscript{−1}), the integrated band intensity, and the depolarization values (\(\rho\)) are given.

\textsuperscript{A}Fermi doublet
molecules in the first sphere without and with a polarizable continuum are summarized in Table 5. Again, the DFT frequencies for the DCOO$^-$·5H$_2$O cluster with a polarizable continuum compare favorably with the measured ones. Finally, a detailed list of all calculated

![Fig. 2 A, B Overview Raman spectrum in R-format (polarized, depolarized, and isotropic) of a 9.459 mol·L$^{-1}$ Na-formate solution at 23 °C. Panel A: Wavenumber range from 50 to 2000 cm$^{-1}$. Inset shows $\nu_2$, the symmetric stretching –COO$^-$ and $\nu_6$, the in-plane C–H deformation mode at full scale (1250 to 1450 cm$^{-1}$). Note, the water deformation band at 1650 cm$^{-1}$ is indicated with an asterisk. Panel B: The C–H stretching band doublet of HCOO$^-(aq)$ at 2732 cm$^{-1}$ and 2818 cm$^{-1}$ due to Fermi resonance of $\nu_1$ with the overtone 2$\nu_6$. The broad and strong O–H stretching band profile of water located at higher wavenumbers with a band maximum at 3432 cm$^{-1}$. The weak band at 2129 cm$^{-1}$ is due to the overtone 2$\nu_4$ and the one at 2973 cm$^{-1}$ to the combination $\nu_5+\nu_6$.](image-url)
DFT frequencies and depolarization values starting with the bare HCOO$^-$ ion, the HCOO$^-$ in a polarizable structureless continuum, and clusters with $n = 1$–5 water molecules and the cluster with 5 H$_2$O in the first sphere plus one water molecule in the outer sphere is given in Table S4. The DFT data in this Table reflect that an increasing number of water molecules in the first sphere of HCOO$^-$ improve the quality of the frequency calculations. The cluster with 5 water molecules in the first sphere and one water in the second does not give a significant improvement compared to the cluster with 5 water molecules.
The experimental Raman band positions (in cm$^{-1}$) and depolarization values ($\rho$) for HCOO$^-$ (aq) (see Table 3) are compared with the simulation results from our DFT calculations using B3LYP/6-311++G(3df,2pfd) for the HCOO$^-$ in vacuo, with solvation (PCM) and the cluster HCOO$^-$·5H$_2$O with and without solvation (PCM).

| Mode        | Approximate Normal Vibration                  | Experimental Raman data | HCOO$^-$ in vacuo$^B$ | HCOO$^-$ + solvation$^B$ | Cluster$^C$ HCOO$^-$·5H$_2$O | Cluster$^C$ HCOO$^-$·5H$_2$O + solvation |
|-------------|-----------------------------------------------|-------------------------|------------------------|--------------------------|-----------------------------|------------------------------------------|
| $\nu_3$     | OCO scissor mode                              | 762 0.33                | 746.9 0.05             | 743.6 0.03               | 766.1 0.56                  | 765.5 0.56                              |
| $\nu_4$     | C–H out-of plane deformation                  | 1066 0.73               | 1045.7 0.75            | 1063.3 0.75              | 1072.5 0.74                 | 1079.9 0.74                             |
| $\nu_5$     | C–O sym. stretch                              | 1350.0 0.13             | 1342.5 0.61            | 1350.7 0.63              | 1378.3 0.29                 | 1367.5 0.21                             |
| $\nu_6$     | C–H in-plane deformation                      | 1382 0.42               | 1374.1 0.75            | 1384.9 0.75              | 1403.4 0.62                 | 1404.4 0.52                             |
| $\nu_5$     | C–O antisym. stretch                          | 1585 0.62               | 1660.4 0.75            | 1590.1 0.75              | 1633.3 0.72                 | 1588.9 0.72                             |
| $\nu_1$     | C–H stretch $^h$                              | 2731 0.26               | 2567.4 0.28            | 2775.9 0.28              | 2875.2 0.32                 | 2920.0 0.31                             |

$^A$The $\nu_1$ C–H mode appears as a Fermi doublet and the undisturbed wavenumber amounts to 2784.7 cm$^{-1}$

$^B$HCOO$^-$ in vacuo possesses C$_{2v}$ symmetry as well as for the polarizable structureless continuum

$^C$The symmetry for formate in both clusters is C$_1$
Table 5  The experimental Raman band positions (in cm⁻¹) and depolarization values (ρ) for DCOO⁻(aq) (see Table 3) are compared with the simulation results from our DFT calculations using B3LYP/6-311++G(3df,2pfd) for the DCOO⁻ in vacuo, with solvation (PCM) and the cluster DCOO⁻·5H₂O with and without solvation (PCM)

| Mode | Approximate Normal Vibration | Experimental Raman data | DCOO⁻ in vacuo | DCOO⁻ + solvation | Cluster A B | Cluster C B | Cluster C C |
|------|-----------------------------|------------------------|----------------|------------------|------------|------------|------------|
|      |                             | Band Position | ρ | Peak Position | ρ | Peak Position | ρ | Peak Position | ρ |
| ν₃   | OCO scissor mode            | 755            | 0.42 | 739.5       | 0.04 | 736.1       | 0.03 | 762.0       | 0.65 | 764.8       | 0.58 |
| ν₄   | C–D out-of plane deformation | 912            | 0.72 | 904.9       | 0.75 | 914.5       | 0.75 | 919.4       | 0.74 | 923.6       | 0.74 |
| ν₂   | C–O sym. stretch            | 1323.8         | 0.08 | 1329.5      | 0.68 | 1332.7      | 0.48 | 1355.7      | 0.19 | 1345.2      | 0.14 |
| ν₆   | C–D in-plane deformation    | 1022           | 0.62 | 1007.4      | 0.75 | 1018.3      | 0.75 | 1031.8      | 0.74 | 1035.7      | 0.74 |
| ν₅   | C–O antisym. stretch        | 1580           | 0.64 | 1656.1      | 0.75 | 1583.4      | 0.75 | 1626.5      | 0.68 | 1576.5      | 0.65 |
| ν₁   | C–D stretch                 | 2030           | 0.33 | 1876.88     | 0.30 | 2019.5      | 0.31 | 2116.8      | 0.37 | 2151.3      | 0.36 |

A The ν₁ C–D mode appears as a Fermi doublet and the undisturbed wavenumber (ν₁) amounts to 2101 cm⁻¹
B DCOO⁻ in vacuo possesses Cᵥ symmetry as well as for the polarizable structureless continuum
C The symmetry of formate in both clusters is C₁
At the terahertz region of the Raman spectrum, the symmetric stretch $\text{Na}^+–\text{OH}_2$ appears as a broad and very weak band at $\approx 189$ cm$^{-1}$ in the isotropic R-spectrum in concentrated NaHCOO solutions at 9.459 mol·L$^{-1}$ (Fig. 5) and a broad band at $\approx 256.5$ cm$^{-1}$ due to the strong H-bonds between HCOO$^-$ and water. In addition, a concentration plot in Fig. S4 is presented for four isotropic Raman spectra of NaHCOO(aq) from 9.245 mol·L$^{-1}$ to 0.732 mol·L$^{-1}$. The breathing mode of the hydrated $\text{Na}^+$, $[\text{Na(OH}_2\text{n}]^+$ with $n = 4–5$, has been observed in NaNO$^3$(aq) solutions as well and a detailed account is given in Ref. [11] including the DFT frequencies. The restricted translations of the H-bonds between $–\text{COO}^-$ and (hydrated) water at 256.5 cm$^{-1}$ in NaHCOO(aq) were also detected for the $–\text{COO}^-$ group in acetate solutions such as $\text{CH}_3\text{COO}^–\cdots\text{HOH}$ [24].

The intramolecular vibrational modes of the formate are found above 700 cm$^{-1}$ in the wavenumber range of the librational water bands (300–900 cm$^{-1}$). The Raman spectral data on NaHCOO(aq) and NaDCOO(aq) such as peak position, fwhm, and integrated band area of the isotropic scattering mode are given in Table 3. Starting with the scissor mode, $\nu_3$ of the carboxylate group arises at 762 cm$^{-1}$. This mode is fairly broad and the band is polarized. In DCOO$^–$(aq), this mode appears at 755 cm$^{-1}$ and is also polarized. The band position of $\nu_3$ for HCOO$^–$(aq) is concentration dependent, and in concentrated NaHCOO(aq) solutions, the mode shifts to slightly higher wavenumbers from 762 cm$^{-1}$ in dilute solution to 766 cm$^{-1}$ in the concentrated solution at 9.254 mol·L. In the saturated solution at 9.459 mol·L$^{-1}$, $\nu_3$ appears at 967 cm$^{-1}$ as a somewhat asymmetric band. All three scattering profiles, $R_{\text{VV}}, R_{\text{VH}},$ and $R_{\text{iso}}$ for the 9.459 mol·L$^{-1}$ solution in the low wavenumber region/terahertz spectral region are given in Fig. S5 showing the restricted H-bond region of the solute, namely water, and the $\nu_3$ mode of HCOO$^–$(aq). However, this mode is fairly weak and therefore harder to detect in dilute solutions.

The C–H out-of-plane deformation mode, $\nu_4$ appears at 1066 cm$^{-1}$ as a narrow band which shows no significant concentration dependence. Its depolarization degree is 0.73. In
the spectrum for DCOO\(^{-}\)(aq), this mode is markedly shifted due to the vibrational isotope effect and appears at 913 cm\(^{-1}\) as a weak band slightly polarized with \(\rho = 0.72\).

The symmetric stretch of the carboxylate group, \(\nu_2\), manifests itself at 1350.0 cm\(^{-1}\) as a strongly polarized band but only moderately strong in infrared [27]. In NaDCOO(aq), this band appears at 1323.8 cm\(^{-1}\) also polarized with \(\rho = 0.08\) and quite narrow with a fwhm = 8.65 cm\(^{-1}\). For both ions, HCOO\(^{-}\) and its deuterated analog DCOO\(^{-}\), the \(\nu_2\) COO\(^{-}\) is the most prominent band in the scattering spectra (Figs. 2 and 3). Its Raman peak position shifts to higher wavenumbers with increasing solute concentration accompanied by an increase of its full width at half maximum (fwhm). This effect was observed in both solutions, NaHCOO(aq) and NaDCOO(aq). A concentration plot of isotropic Raman scattering profiles of the symmetric stretching mode of HCOO\(^{-}\), \(\nu_2\), is given in Fig. 6A, together with the C–H in-plane mode, \(\nu_6\), which overlaps \(\nu_2\) –COO\(^{-}\) slightly. The C–H in-plane deformation mode, \(\nu_6\), arises at 1382 cm\(^{-1}\) as a weak, polarized band quite insensitive to the solute concentration. In the scattering spectrum for DCOO\(^{-}\)(aq), this mode shifts considerably to lower wavenumbers and was observed at 1022 cm\(^{-1}\) also polarized and leaves the \(\nu_2\) mode, \(\nu_5\) –COO\(^{-}\) as a single band. A concentration plot of the \(\nu_2\) mode of –COO\(^{-}\), symmetric stretch is shown Fig. 6B. In NaDCOO(aq) solutions, a slight shift to higher wavenumbers of the \(\nu_2\) mode and an increase of the fwhm from the dilute solution at 0.0718 mol·L\(^{-1}\) to
the concentrated one at 3.950 mol·L\(^{-1}\). Finally, it should be noted that the \(\nu_2\) –COO\(^{-}\) band in DCOO\(^{-}\)(aq) contains a very weak shoulder at \(~1303\) cm\(^{-1}\) (Fig. 6B). The abundance of the isotopomer is 0.4 mol\%. In HCOO\(^{-}\)(aq) solution, the \(\nu_2\) –COO\(^{-}\) band does not allow the observation of the isotopomer because of the naturally broad band shape which is twice as large as the one in DCOO\(^{-}\)(aq). In Table S5 A and B, the band parameters of the \(\nu_2\) –COO\(^{-}\) mode in HCOO\(^{-}\)(aq) and DCOO\(^{-}\)(aq) are given.

The antisymmetric stretch of the –COO\(^{-}\) group, \(\nu_5\), appears at 1585 cm\(^{-1}\) in dilute solution but is polarized with \(\rho=0.62\). The band of \(\nu_5\) –COO\(^{-}\) is quite broad and fairly weak. In the infrared spectrum, the \(\nu_5\) mode is the strongest band of the NaHCOO(aq) solution and appears at ~1580 cm\(^{-1}\) [27]. In DCOO\(^{-}\)(aq) \(\nu_5\), the antisymmetric stretch of –COO\(^{-}\) appears at 1580 cm\(^{-1}\) in the Raman effect as a fairly broad band and this band is also polarized.

Finally, the C–H stretching mode, \(\nu_1\), presents itself as a double mode with peak positions at 2730 and 2820 cm\(^{-1}\) and the band components are polarized. It is noteworthy that the DFT frequency from the cluster HCOO\(^{-}\)·5H\(_2\)O for the C–H stretch gives only a single value at 2875.2 cm\(^{-1}\). In fact, only one single C–H stretch results from all the applied DFT models (Tables 4 and S4). As mentioned above, in the infrared spectrum of HCOO\(^{-}\)(aq) in a neon matrix, only one single weak band was reported for \(\nu_1\) at 2455.7 cm\(^{-1}\). The band doublet in HCOO\(^{-}\)(aq) is a result of Fermi resonance of the first overtone of \(2\nu_6\) with \(\nu_1\). The undisturbed wavenumber value for \(\nu_1\) in water for HCOO\(^{-}\) lies at 2784.7 cm\(^{-1}\). In HCOO\(^{-}\)(D\(_2\)O), the formate in heavy water (see results in Table S2), the undisturbed wavenumber amounts to 2780.7 cm\(^{-1}\). The environmental effect in D\(_2\)O(l) causes a small but noticeable effect. In the NaDCOO(aq) spectrum, a band doublet appears at much lower wavenumber values compared to the one in HCOO\(^{-}\)(aq) due to the large vibrational isotope effect. The band positions appear at 2030 cm\(^{-1}\) and 2116.5 cm\(^{-1}\), and these bands are also polarized (Fig. 3). The undisturbed wavenumber value for \(\nu_1\) C–D in water for DCOO\(^{-}\) in aqueous solution lies at 2101 cm\(^{-1}\). The undisturbed mode was calculated [28] by taking a two-level Fermi resonance model into account and assuming that the perturbed and unperturbed modes are centered around a common average value [29]. In addition to the Fermi resonance doublet of \(\nu_1\), weak Raman bands were observed at 2129 cm\(^{-1}\) (\(2\nu_4\)) and 2973 cm\(^{-1}\) (\(\nu_3+\nu_5\)) in NaHCOO(aq). These bands were identified as overtone/combination bands. In DCOO\(^{-}\)(aq), weak bands appear at 1825.4 cm\(^{-1}\) (\(2\nu_4\)) and 2078 cm\(^{-1}\) (\(\nu_2+\nu_3\)) in addition to the fundamental normal modes and both bands are polarized.

### 3.3 Comparison of \(\nu_s\) COO\(^{-}\) and \(\nu_as\) COO\(^{-}\) of HCOO\(^{-}\)(aq) with CH\(_3\)COO\(^{-}\)(aq)

In the Raman scattering of HCOO\(^{-}\) solutions, the symmetric stretch appears as the strongest band at 1350 cm\(^{-1}\) (fwhm = 13.1 cm\(^{-1}\)) and the antisymmetric stretch at 1585 cm\(^{-1}\) as a fairly weak band but broad (fwhm = 43 cm\(^{-1}\)). The \(\nu_s\) COO\(^{-}\) band is polarized with \(\rho=0.125\) and the antisymmetric stretch \(\nu_as\) COO\(^{-}\) is partially polarized (\(\rho=0.62\)). The difference of the wavenumbers of antisymmetric stretch minus the symmetric stretch, \(\Delta=\nu_as\) COO\(^{-}\) – \(\nu_s\) COO\(^{-}\), is a measure for the state of the –COO\(^{-}\) group and the delta value for HCOO\(^{-}\)(aq) is 235 cm\(^{-1}\). In infrared absorption, the symmetric stretching band manifests itself as a medium to strong absorption mode at 1351 cm\(^{-1}\), while the antisymmetric stretch at ~1580 is very strong [27]. (The published band maxima in infrared vary somewhat [4, 8, 27]). Recent published Raman band maxima for acetate, CH\(_3\)COO\(^{-}\)(aq) [26], revealed \(\nu_s\) COO\(^{-}\) at 1413.5 cm\(^{-1}\) (\(\rho=0.260\)) and for \(\nu_as\) COO\(^{-}\) at 1556 cm\(^{-1}\) (\(\rho=0.62\)) and a \(\Delta\)-value for CH\(_3\)COO\(^{-}\)(aq) amounts to 142.5 cm\(^{-1}\), much smaller than the aforementioned
value for HCOO\(^{-}\)(aq). It should be stressed that the band position of the scissor mode is also quite sensitive to the state of HCOO\(^{-}\) in the gas phase, hydration state, and ion pairing and may be used for assignment purpose [24].

From the DFT optimization applying the polarizable continuum model for HCOO\(^{-}\) (C\(_2v\) symmetry) which reflects the solution state, resulted in a bond length for both C–O bonds at 1.252 Å and an angle of the CO\(^{-}\) moiety at 128.31\(^\circ\). These results compare with the ones published earlier on acetate CH\(_3\)COO\(^{-}\), also with solvation (PCM) [24], resulted in two different C–O bond lengths at 1.261 Å and at 1.259 Å (C\(_s\) symmetry) and an angle at 125.4\(^\circ\). The average value for the bond length of the two C–O bonds in acetate is larger than the one in HCOO\(^{-}\). The DFT frequencies for HCOO\(^{-}\) with solvation (PCM) resulted in values for \(\nu\)\(s\)COO\(^{-}\) at 1350.7 cm\(^{-1}\) and for \(\nu\)\(as\)COO\(^{-}\) at 1590.1 cm\(^{-1}\). The DFT frequencies for the acetate with solvation (PCM) for the corresponding modes gave values at 1397.4 cm\(^{-1}\) and 1557.4 cm\(^{-1}\), respectively [24, 26]. The application of the PC model despite the non-directional continuum approach leads to quite realistic frequencies of the symmetric and antisymmetric stretch of the –COO\(^{-}\) group for both molecule ions HCOO\(^{-}\) and CH\(_3\)COO\(^{-}\).

The symmetry of the two ions as bare ions in vacuo and with PCM applied leads to C\(_2v\) and C\(_s\), respectively. The application of the discrete cluster model with five water molecules in the first hydration sphere, the COO\(^{-}\) moiety in HCOO\(^{-}\) (Tables 1 and 2 for geometry and frequencies) and in CH\(_3\)COO\(^{-}\) (frequencies in Table 2 Ref. [26] and geometric data see Table 1 in Ref. [24]) also gave quite realistic frequencies but the symmetry of both ions changed to C\(_1\) due to hydration. It is noteworthy that the calculated depolarization values of the bands gave fair results compared with the measured ones as well. The cluster HCOO\(^{-}\) with 5 water molecules in the first sphere resulted for \(\nu\)\(s\)COO\(^{-}\) and \(\nu\)\(as\)COO\(^{-}\) at 1378 cm\(^{-1}\) and 1633.3 cm\(^{-1}\). A similar cluster model for CH\(_3\)COO\(^{-}\) with \(n = 5\) water molecules gave the corresponding frequencies at 1418.6 cm\(^{-1}\) and 1612 cm\(^{-1}\).

Finally, it should be stressed that the discrete cluster model with five water molecules HCOO\(^{-}\)·5H\(_2\)O was placed in a polarizable structureless continuum in order to extend the hydration effect of water combining the discrete cluster model with PCM. The results are given in Table 1 for the geometry parameters and in Table 4 for the frequencies as well as depolarization values of the HCOO\(^{-}\) bands. Such an approach leads to an even better description of the intramolecular HCOO\(^{-}\) bands.

In a spectroscopic study on carboxylates, Spinner [30] invoked two different resonance structures for the COO\(^{-}\) group and claimed that these structures are in equilibrium with one another, and therefore, the COO\(^{-}\) group is not a symmetric one but has two differently bonded oxygen atoms in equilibrium with one another. However, resonance structures are not equilibrium structures but they describe delocalized electrons that cannot be expressed by a single Lewis formula with an integer number of covalent bonds. From a quantum chemical point of view, Spinner’s explanation has to be rejected.

### 3.4 Ion Pairing in NaHCOO(aq) and LiHCOO(aq)

In dilute solutions up to ~1.0 mol·L\(^{-1}\), NaHCOO(aq) spectra show only very small changes in their Raman band parameters such as peak position and fwhm in contrast to the findings in concentrated NaHCOO(aq) solutions. The structure in dilute solutions may be described as water-like, while the concentrated ones are melt-like [31, 32]. The concentration study demonstrates that hardly any ion pairing in dilute to moderately concentrated solutions occurs in NaHCOO(aq). The peak of the \(\nu\)\(s\)COO\(^{-}\) mode shifts to higher wave-numbers with concentration increase and this peak shift is accompanied with a broadening
of the mode (Table S5 A). The antisymmetric stretch, ν\textsubscript{as}COO\textsuperscript{−}, weak and broad in appearance, is also concentration sensitive and occurs in dilute solution at 1586 cm\textsuperscript{-1} and for a saturated solution (9.459 mol·L\textsuperscript{-1}) at 1596 cm\textsuperscript{-1}. The COO\textsuperscript{−} scissor mode, ν\textsubscript{3}, also shifts to higher wavenumbers from 762 cm\textsuperscript{-1} in dilute solutions to 767 cm\textsuperscript{-1} in the saturated solution at 9.459 mol·L\textsuperscript{-1} accompanied by a considerable widening of the band and also a slight asymmetry. The dependence of the peak maximum and the fwhm of the symmetric stretching mode ν\textsubscript{2} COO\textsuperscript{−} is plotted in Fig. 7 against the molar ratio of water to solute (R\textsubscript{w}-value). The graph reveals that in going from high concentrations, i.e., low R\textsubscript{w} with a value at 20, the curve flattens considerably and at 50 the graph levels off. The two slopes of the curve meet at R\textsubscript{w}-value ~ 26 which corresponds to a concentration ~ 2 mol·L\textsuperscript{-1}. The graph demonstrates that at least two species contribute to the fwhm of the ν\textsubscript{2} COO\textsuperscript{−} mode, namely, outer-sphere ion pairs with one interposed water molecule between Na\textsuperscript{+} and HCOO\textsuperscript{−} and fully hydrated species.

Fig. 7 Dependence of peak position (upper panel) and fwhm (lower panel) of the symmetric stretching mode ν\textsubscript{2} −COO\textsuperscript{−} from the molar ratio of water to solute (R\textsubscript{w}-value). At a R\textsubscript{w}-value at 20, the curves flatten, and at a value at 50, the curves are leveling off. On the upper x-axis of the upper panel, the solute concentrations corresponding to R\textsubscript{w} values are given. The two slopes of the curves meet at R\textsubscript{w}-value ~ 25 which corresponds to a concentration ~ 2 mol·L\textsuperscript{-1}. The graph demonstrates that at least two species contribute to the fwhm of the ν\textsubscript{2} COO\textsuperscript{−} mode, namely, outer-sphere ion pairs with one interposed water molecule between Na\textsuperscript{+} and HCOO\textsuperscript{−} and fully hydrated species.
water to NaHCOO equal to ~4.2. The optimized cluster \( \text{Na}^+(\text{H}_2\text{O})_4\text{HCOO}^- \) (Fig. 8) gives realistic frequencies and geometries which compare well with the solution spectra at such a concentrated NaHCOO\(^-\) solution. The bond distance of Na\(^+\) closest to one of the oxygen atoms of HCOO\(^-\), O\(_{\text{formate}}\), shows direct contact and a bond distance at 2.322 Å, signifying a monodentate bonding (Fig. 8). Complete geometrical parameters for the cluster are given in Table S6. It has to be stressed that the presented cluster is only one of many possible clusters in these concentrated solutions. The structures are somewhat flexible in solution state. A description of these flexible structural arrangements for aqueous acetate solutions (bond angles, bond lengths) is given in Ref. [33].

Measurements on a 0.732 mol·L\(^{-1}\) NaHCOO solution with increasing amounts of LiCl, 4.028 and 8.420 mol·L\(^{-1}\), display marked influence of the Li\(^+\) ion on the \( \nu_2 \) mode, \( \nu_5 \) COO\(^-\), and the \( \nu_3 \) or scissor mode. Both modes shift considerably to higher wavenumbers compared to the solution without LiCl present, and simultaneously, the band width of the modes increases to a large extent. In Fig. 9, the Raman scattering profiles of these solutions are given at 0.732 mol·L\(^{-1}\) without LiCl added as profile (1) and with 4.028 mol·L\(^{-1}\) LiCl as profile (2) and with 8.420 mol·L\(^{-1}\) as profile (3). In Fig. S7, the Raman scattering profiles of a 0.732 mol·L\(^{-1}\) with added LiCl at 8.420 mol·L\(^{-1}\) is shown in a larger wavenumber range from 700 to 2200 cm\(^{-1}\). The \( \nu_2 \) COO\(^-\) mode appears in this solution at 1358 cm\(^{-1}\).

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2 The presented ATR FTIR spectral bands of \( \nu_5 \) –COO\(^-\) and \( \nu_{as} \) –COO\(^-\) for aqueous alkaline metal acetate solutions in Ref. [33] are obviously not corrected for polarization and the penetration depth, \( dp \), and the same criticism applies to the one raised under the first footnote. Bands from ATR FTIR measurements do not reflect the true absorption bands [17]. The correct sequence of the wavenumber shift to larger values of the –COO\(^-\) symmetric stretching mode with solute concentration increase in these solutions has to be Li\(^+\) > Na\(^+\) > K\(^+\) > Rb\(^+\) > Cs\(^+\).
as a broad band with almost twice the fwhm compared to the one without LiCl and the COO− scissor mode, $\nu_3$, appears as an asymmetric band at 776 cm$^{-1}$ which may be fitted with two component bands at 777.4 cm$^{-1}$ and a smaller band component at 760 cm$^{-1}$ (Fig. S8). Such a significant shift of the scissor mode $\nu_3$ to higher wavenumbers shows that the force constant of the bending mode is getting larger. In solutions with a large mole ratio Li$^+$ to HCOO$^-$, the formate forms contact ion pairs not only with a 1:1 stoichiometry, [Li(HCOO$^-$)]$^{0}$aq but also with 2:1 stoichiometry as [Li$_2$(HCOO)$^+$aq.

In order to give a realistic structural picture of the hydration behavior in such a concentrated solution, a Li$^+$(H$_2$O)$_4$HCOO$^-$ cluster was calculated. In this solution containing large amounts of Li$^+(aq)$ in which direct contact with HCOO$^-$ is forced by the low molar ration water to solute, the bond distance of Li$^+$ and one of the oxygen atoms of HCOO$^-$, O$_{\text{Formate}}$, is at 1.969 Å even smaller compared to the one in the Na$^+−$H$_2$O$−$HCOO$^-$ cluster (complete geometry data of this cluster see Table S6). Again, a monodentate bonding between Li$^+$ and O$_{\text{Formate}}$ is realized and the structure of the Li$^+$(H$_2$O)$_4$HCOO$^-$ is given.

In concentrated NaHCOO solutions or solutions with a high mole ratio Li$^+$ to HCOO$^-$ in which ion pairing is forced into closer contact up to the point where not enough water molecules constitute the solution, direct contact between M$^+$ and HCOO$^-$ occurs. The outer-sphere ion pairs and the contact ion pairs are caused by the lack of water molecules at such a concentration state. In dilute solutions, in contrast, the ions are fully hydrated and a hydration number of ~5 was found for HCOO$^-$ at solution concentrations C $\rightarrow$ 0 mol·L$^{-1}$.

The discussion of the ion pairing with concentration increase of alkali metal acetates (0.25 to 4.00 mol·L$^{-1}$) was modeled, recently, applying high-level quantum chemical
The simulation results on structures of solvent separated ion pairs and contact ion pairs revealed a variety of structural forms and resulted in varying vibrational frequencies. Furthermore, it was deduced as a result of the simulations that ion pairing must occur at solute concentrations at 1 to 2 mol·L⁻¹ slightly depending on the nature of the alkali metal ion. These results support our Raman spectroscopic findings and qualitative discussions on ion pairing which clearly depends on the solution concentration.

4 Conclusions

NaHCOO(aq) and NaDCOO(aq) solutions were measured applying Raman spectroscopy from the dilute to the concentrated solution state including a saturated solution and a solution in heavy water. Band parameters such as peak position, fwhm, integrated intensity, and depolarization values were determined. The mode, ν₂, the symmetric stretch –COO⁻ is the most prominent band in the Raman spectrum in the solutions of HCOO⁻(aq) and in DCOO⁻(aq). The ν₆ mode, the C–H in-plane deformation at 1382 cm⁻¹ in HCOO⁻(aq) shifts with deuteration to 1022 cm⁻¹ in DCOO⁻(aq) and leaves ν₂ as a single narrow band at 1323.8 cm⁻¹. The isotopomer of D¹⁸O¹⁶O⁻(aq) with an abundance of 0.4 mol% appears as a very weak shoulder at 1303 cm⁻¹. Furthermore, from the Raman spectroscopic data, it was concluded that the HCOO⁻(aq) symmetry is neither C₂ᵥ nor C₃ but C₁. DFT frequency calculations confirm the band assignments and depolarization values drawn from the Raman spectroscopic data applying cluster calculations of HCOO⁻ and implicit water molecules. In contrast to the Raman spectrum of NaHCOO(aq) solution, where the C–H stretch appeared as a band doublet at 2730 and 2820 cm⁻¹, only one DFT frequency could be obtained at ~2800 cm⁻¹ (at 2772.4 cm⁻¹ (PCM)). The observed doublet is due to Fermi resonance of the overtone of the bending C–H mode, ν₆ at 1382 cm⁻¹ with ν₁ and the undisturbed band appears at 2785 cm⁻¹. The Fermi doublet in NaDCOO(aq) appears at 2030 cm⁻¹ and 2116.5 cm⁻¹ and the undisturbed wavenumber (ν₁) amounts to 2101 cm⁻¹. Furthermore, a solution of HCOO⁻ in D₂O showed slightly changed frequencies compared with the ones in water and is caused by the solvent isotope effect also observed for CH₃COO⁻ in H₂O and D₂O.

Ion pairs between Na⁺ and HCOO⁻ characterize the Raman spectrum at high solute concentrations. Added LiCl to NaHCOO(aq) shows the large perturbation of the HCOO⁻ bands especially the νₛCOO⁻ and δ COO⁻ bands of HCOO⁻ and reveals a strong affinity of Li⁺ toward HCOO⁻ compared to Na⁺. The ion pairs formed are most likely contact ion pairs between Li⁺ and HCOO⁻ which have different stoichiometry of Li⁺: HCOO⁻ such as 1:1 and 2:1.

Comparison of νₛ COO⁻ mode of formate and acetate shows that in HCOO⁻(aq) νₛ at 1350 cm⁻¹ is much smaller than the one in acetate which amounts to 1415 cm⁻¹. Furthermore, the symmetric stretch of the –COO⁻ group is strong in the Raman effect but only moderately strong in infrared. In infrared absorption, the antisymmetric stretch of COO⁻ is very strong but weak in the Raman effect.

Appendix A

See Table 6.
Table 6  Electronic energy, thermal energy, and entropy of the anion HCO$_2^-$ and several clusters with H$_2$O derived from DFT calculations [B3LYP/6-311++G(3df,2pfd)]

| parameter | HCO$_2^-$ in vacuo | HCO$_2^-$·H$_2$O | HCO$_2^-$·2H$_2$O | HCO$_2^-$·3H$_2$O | HCO$_2^-$·4H$_2$O | HCO$_2^-$·5H$_2$O | HCO$_2^-$·5H$_2$O·H$_2$O |
|-----------|--------------------|------------------|------------------|------------------|------------------|------------------|--------------------------|
| $E_{\text{electron}}$/Hartree | $-189.284$ | $-265.777$ | $-342.266$ | $-418.752$ | $-495.234$ | $-571.715$ | $-648.197$ |
| $E_{\text{thermal}}$/kJ·mol$^{-1}$ | $60.14$ | $133.90$ | $207.44$ | $282.86$ | $356.44$ | $428.84$ | $502.82$ |
| $S$/J·K$^{-1}$·mol$^{-1}$ | $238.49$ | $312.38$ | $375.64$ | $415.62$ | $492.40$ | $598.63$ | $639.09$ |
| $\Delta H_n$/kJ·mol$^{-1}$ | $-67.928$ | $-123.74$ | $-171.98$ | $-211.13$ | $-250.93$ | $-288.67$ |
| $\Delta H_n - \Delta H_n$ experiment/kJ·mol$^{-1}$ | $-67.928$ | $-55.808$ | $-48.24$ | $-39.15$ | $-39.80$ | $-37.64$ |

In addition to the binding enthalpy $\Delta H_n$ of the clusters, a comparison is given with the few available experimental values (see Refs. [19, 20]) of reaction enthalpies $\Delta H_n$

$^a$1 Hartree is equivalent to 2625.5 kJ·mol$^{-1}$
The binding enthalpy of the cluster with $nH_2O$ was calculated according to 
\[ \Delta H_n = H_{HCO^- \cdot nH_2O} - H_{HCO^-} - n \cdot H_{H_2O} \quad (n = 1–5). \]
The difference of binding enthalpies $\Delta H_n - \Delta H_{n-1}$ can then be compared with experimental values for the few reaction enthalpies $\Delta rH_n$ obtained with TDAS (thermal detection-mass spectrometry) [19, 20] and the following reaction equilibria were considered:

1. $HCOO^- + H_2O \rightleftharpoons HCOO^- \cdot H_2O$ (7)
2. $HCOO^- \cdot H_2O + H_2O \rightleftharpoons HCOO^- \cdot 2H_2O$ (8)
3. $HCOO^- \cdot 2H_2O + H_2O \rightleftharpoons HCOO^- \cdot H_2O$ (9)

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Declarations

Conflict of interest The authors declare that they have no competing financial interest.

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