



Vibrational spectroscopic studies and DFT calculations on tribromoacetate and tribromoacetic acid in aqueous solution

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ABSTRACT

Aqueous solutions of sodium tribromoacetate ($\text{NaCBr}_3\text{CO}_2$) and its corresponding acid (CBr_3COOH) have been studied using Raman and infrared spectroscopy. The spectra of the species in solution were assigned according to symmetry C_s . Characteristic bands of $\text{CBr}_3\text{CO}_2^-$ (aq) and the tribromoacetic acid, CBr_3COOH (aq), are discussed. For the hydrated anion, the CO_2 group, the symmetric CO_2 stretching mode at 1332 cm^{-1} and the asymmetric stretching mode at 1651 cm^{-1} are characteristic while the $\text{C}=\text{O}$ mode at 1730 cm^{-1} is characteristic for the spectra of the acid. The stretching mode, $\nu\text{C}-\text{C}$ at 912 cm^{-1} for $\text{CBr}_3\text{CO}_2^-$ (aq) is 10 cm^{-1} lower in the anion compared with that of the acid. These characteristic modes are compared to those in acetate, CH_3CO_2^- (aq). Coupling of the modes are fairly extensive and therefore DFT calculations have been carried out in order to compare the measured spectra with the calculated ones. The geometrical parameters such as bond length and bond angles of the tribromoacetate, and tribromoacetic acid have been obtained and may be compared with the ones published for other acetates and their conjugated acids.

CBr_3COOH (aq) is a moderately strong acid and the $\text{p}K_a$ value derived from quantitative Raman measurements is equal to -0.23 at 23°C . The deuterated acid CBr_3COOD in heavy water has been measured as well and the assignments were given.

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1. Introduction

Metal acetates are used in many industrial processes, in food preservation, as mordants for textile printing and dyeing, as additives in lubricating oils and greases, as catalysts and intermediates in organic reactions, and as pigments for ceramics, to name a few [1]. Furthermore, acetates and the haloacetates (the latter term refers to fluoro-, chloro- and bromo-acetates) exist widely in the biosphere. These compounds arise from photochemical degradation of halogenated hydrocarbons from direct anthropogenic emissions and also natural sources [2,3].

Recent interest in studying carboxylates and carboxylic acids in aqueous solution stems from their importance as constituents in biomolecules such as amino acids, fatty acids and surfactants among others [4]. Detailed studies aimed at the hydration, dissociation and ion-pair formation of these species in solution have been carried out by infrared [4–6] and dielectric relaxation spectroscopy (DRS) [7,8]. DRS studies are especially useful in determining hydration numbers and association constants in salt solutions forming ion pairs between anions and cations (solvent

shared-, solvent–solvent separated ion pairs and ion pairs without interposed water). Such studies have been carried out on aqueous solutions of sodium salts of dicarboxylates such as oxalate, malonate and succinate [7,8]. Although acetates and haloacetates have been studied quite frequently by vibrational spectroscopy [4–6,9] surprisingly, such is not the case for tribromoacetate and tribromoacetic acid. While one early vibrational spectroscopic study emphasized the investigation of potassium tribromoacetate and tribromoacetic acid in the solid state only a few incomplete solution spectra were given [10]. Infrared and Raman spectra of $\text{NaCBr}_3\text{CO}_2$ in the solid state have been reported as part of a vibrational spectroscopic investigation of substituted acetates in Ref. [9].

As part of a speciation study on haloacetates and their corresponding acids in aqueous solution as well as the lack of complete data on the tribromoacetate and the tribromoacetic acid prompted us to report on the vibrational spectra of CBr_3COOH (aq) and its corresponding anion $\text{CBr}_3\text{CO}_2^-$ (aq). In order to compare the spectroscopic data of the characteristic modes ($\nu\text{C}-\text{C}$, $\nu_3\text{CO}_2$ and $\nu_{\text{as}}\text{CO}_2$) for $\text{CBr}_3\text{CO}_2^-$ (aq) with the ones in the acetate, CH_3CO_2^- (aq), several solutions of sodium acetate have been measured as well. The spectral assignments of the hydrated species are supplemented with DFT calculations in order to guide the assignments of the measured spectra. In addition, the DFT parameters such as bond length and bond angles of the tribromoacetic acid and its salt in

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the gas phase and with a continuum solvation sphere have been reported.

A dilution series of tribromoacetic acid and the addition of HCl to aqueous solutions of tribromoacetic acid suppressing the dissociation allowed for the identification of the bands of $\text{CBr}_3\text{COOH}(\text{aq})$ in addition to the bands of the anion, $\text{CBr}_3\text{CO}_2^-(\text{aq})$. Quantitative Raman data on the concentration dependence of the equilibrium of tribromoacetic acid dissociation as a function of dilution have been collected and the $\text{p}K_a$ value for the tribromoacetic acid dissociation has been calculated. Deuterated solutions of tribromoacetic acid solutions in heavy water have been measured in order to complement the spectroscopic assignments.

2. Experimental

2.1. Preparation of the solutions

Preparation of a $\text{NaCBr}_3\text{CO}_2$ stock solution started with a CBr_3COOH (Aldrich, 99.5%) solution and was neutralized with a slightly higher amount of carbonate free 18.45 M NaOH solution (ca. 2%) than needed. The crystalline acid was purchased from Aldrich (99.5%). The solution was concentrated in a vacuum apparatus and then cooled to 4 °C. The precipitated crystal pulp was filtered through a suction filter and the white crystals were dried at 40 °C for several hours. The solutions have been prepared from $\text{NaCBr}_3\text{CO}_2$ and triply distilled water by weight. A stock solution $\text{NaCBr}_3\text{CO}_2$ 1.927 mol L⁻¹ was prepared and the pH value of the solution pH was measured to ~8.20. Two dilute solutions were prepared from the stock solution: (A) 0.964 mol L⁻¹ and (B) 0.385 mol L⁻¹ $\text{NaCBr}_3\text{CO}_2$ solution.

For purposes of comparison of the CO_2^- modes in solutions of $\text{CH}_3\text{CO}_2^-(\text{aq})$ with the ones of tribromoacetate, stock solutions of NaCH_3CO_2 have been prepared from dried anhydrous NaCH_3CO_2 (99.5% extra pure; Merck, Darmstadt, Germany) with triply distilled water by weight. The following NaCH_3CO_2 solutions have been prepared: 1.209 mol L⁻¹, 0.810 mol L⁻¹ and 0.161 mol L⁻¹.

Aqueous stock solutions of CBr_3COOH , 1.880 mol L⁻¹, and 1.680 mol L⁻¹ were prepared by weight. A CBr_3COOH solution with an excess of HCl was prepared in order to study the undissociated acid (repression of the dissociation). A dilution series of the tribromoacetic acid were prepared by weight and doubly distilled water. Furthermore, a tribromoacetic acid solution in heavy water was prepared from deuterated CBr_3COOD crystals and heavy water by weight. The deuterated tribromoacetic acid was prepared from the light acid which was dissolved in heavy water and subsequently crystallized. This procedure was carried out twice. The solution densities were determined with a pycnometer of 5.000 mL volume at (23 ± 0.1) °C.

2.2. Raman spectra

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. These measurements have been described in detail elsewhere [11,12]. Briefly, however, the spectra were excited with the 487.98 nm line of an Ar⁺ laser at a power level of ~1100 mW at the sample. After passing the spectrometer in subtractive mode, with gratings of 1800 grooves/mm, the scattered light was detected with a cooled CCD detector. I_{VV} and I_{VH} spectra were obtained with fixed polarisation of the laser beam by rotating the polarisator at 90° between the sample and the entrance slit to give the scattering geometries:

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

$$I_{VH} = I(Y[ZY]X) = 3\gamma^2 \quad (2)$$

The isotropic spectrum, I_{iso} or I_α is then constructed:

$$I_{\text{iso}} = I_{VV} - (4/3)I_{VH} \quad (3)$$

The depolarization ratio, ρ , of the modes was determined according to Eq. (4)

$$\rho = I_{VH}/I_{VV} = 3\gamma^2/(45\alpha^2 + 4\gamma^2) \quad (4)$$

The polarisation analyser was calibrated with CCl_4 before each measuring cycle and adjusted if necessary. The depolarization ratio of the ν_1 mode of CCl_4 at 459 cm⁻¹ was measured 15 times and a depolarization ratio equal to 0.0036 ± 0.0005 determined. The depolarization degree of the CCl_4 modes at 217 cm⁻¹ and 315 cm⁻¹ (these modes are depolarised according to the theory) have been determined to 0.75 ± 0.02.

The wavenumber positions have been checked with Neon lines and the peak positions for bands with smaller band width (full width at half height; FWHH) have been determined with an error of ±0.5 cm⁻¹ and broader bands FWHH ≥ 25–30 cm⁻¹ with a precision of ±1 cm⁻¹. The signal to noise ratio for the band at 1332 cm⁻¹ of the spectra for a 0.402 mol L⁻¹ has been determined to 370:1 and was much better for the modes in more concentrated solutions.

Band intensities have been determined by fitting the bands using Gaussian–Lorentzian product functions on baseline corrected spectra. In the case of the tribromoacetic acid solutions, overlap between bands of the tribromoacetic acid and its corresponding salt, $\text{CBr}_3\text{CO}_2^-(\text{aq})$ have been resolved by fitting the band profiles. Band intensities for $\text{CBr}_3\text{CO}_2^-(\text{aq})$, $\text{CBr}_3\text{COOH}(\text{aq})$ and $\text{CBr}_3\text{COOD}(\text{D}_2\text{O})$ have been presented as relative integrated band intensities, I_{rel} . The details of the band fitting procedure of the baseline corrected Raman- and infrared-bands has been described elsewhere [13].

Quantitative Raman measurements have been carried out to determine the dissociation constant of tribromoacetic acid according to an external quantification method previously described [14]. Raman spectra were measured with equipment described above at (23 ± 0.1) °C and the solutions have been measured in quartz cuvettes from Helma. The spectra were excited with the 487.98 nm of an Ar⁺ laser at power levels ~1100 mW and only the I_{VV} scattering has been recorded. The stability of the apparatus has been checked, including the laser power, by measuring the ν_1 mode of SO_4^{2-} of a 0.740 mol L⁻¹ K_2SO_4 solution during the measuring cycle of ~1.5 h. The variation of the integrated band intensity of the external reference mode $\nu_1\text{SO}_4^{2-}$ at 981 cm⁻¹ was better than ±1% during a measuring cycle. The analytical band of $\text{CBr}_3\text{CO}_2^-(\text{aq})$ at 1332 cm⁻¹, $\nu_s\text{CO}_2$ has been chosen because it does not overlap with modes of $\text{CBr}_3\text{COOH}(\text{aq})$ and can therefore be integrated quite easily. Five NaCBr_3COO solutions (0.0107, 0.0265, 0.0651, 0.1617 and 0.401 mol L⁻¹) have been measured in the wavenumber range from 1154 to 1830 cm⁻¹ and four CBr_3COOH solutions (0.402, 0.941, 1.680, and 1.800 mol L⁻¹). The measuring cycle was as follows: first, measurement of the CBr_3COOH solution, second, the $\text{SO}_4^{2-}(\text{aq})$ and then the $\text{NaCBr}_3\text{CO}_2$ solution and so on. Two independent measurements have been carried out. The integrated band intensity, A_{1332} as a function of concentration has been established and from this calibration curve the equilibrium concentration of $[\text{CBr}_3\text{CO}_2^-]$, and $[\text{CBr}_3\text{COOH}]$ determined in the acid solutions ($A_{1332} = 47046.0 \cdot C_{\text{CBr}_3\text{COO}^-}$; $R^2 = 0.9998$). (The equilibrium species concentration i is denoted as $[i]$.) The degree of dissociation α of the acid has been calculated according to $\alpha = [\text{CBr}_3\text{CO}_2^-]/c_T$ with c_T the total acid concentration in the solution.

2.3. Infrared spectra

The infrared solution spectra were measured with the FT-IR spectrometer IFS66v (BRUKER OPTICS, Germany)[9] in the wave-

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