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Formate Ion: Structure and Spectroscopic Properties

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Received: September 1, 2010; Revised Manuscript Received: November 22, 2010

The formate anion $HCOO^-$ is present in a multitude of systems of relevance, and it is characterized by its plasticity, adopting several different structures. This work provides a theoretical study of the ion focused on two of these structures, a crystal and an isolated species. Crystals of sodium formate and ammonium formate are studied using CASTEP, a solid-oriented computing package. Individual molecules of the same systems and of the formate and ammonium ions are also studied, using the Gaussian code at the MP2/aug-cc-pvTZ level. All theoretical calculations are contrasted by comparison to observed infrared spectra, recorded by using different techniques. In addition, a topological analysis of the bonding properties of the isolated molecules is presented.

1. Introduction

The carboxylate ($RCOO^-$) functional group is omnipresent in biology, forming part of all amino acids. The simplest carboxylate, the formate ion $HCOO^-$, is present also in a multitude of systems and could be found, e.g., in natural waters as a result of photooxidation of humic substances.[1] Perhaps one of its most recent and exciting occurrences would be its possible detection in astrophysical ices (see ref 2), especially in relation with spectroscopic features tentatively assigned to their counterion ammonium, NH_4^+, particularly the elusive 6.85 μm band.[3] The astrophysical interest of this species has prompted several recent investigations, of either theoretical[4] or experimental nature,[5] and is also one of the main reasons why we started this research.

One of the peculiarities of the formate ion is the different structure that it can adopt depending on its environment and physical state. This was already a focus of research in the 1930s,[6,7] when a special configuration was proposed for the formate ion in solution, while the so-called normal structure was retained for the acid, its esters, and the formate ion in the crystal.[8] The structure may vary depending also on the cation with which it is associated. X-ray diffraction studies showed that crystalline sodium formate and ammonium formate (refs 8 and 10, respectively) present different configurations, with possible resonant structures in the former and H-bonding between O and N atoms in the latter. We are not aware of theoretical calculations of these systems as solid crystals, although other theoretical and spectroscopic studies of species containing the formate ion have been reported over the years (see, for instance, ref 11 for work on calcium formate crystals, ref 12 for lithium formate monohydrate, and ref 13 for solid amino formate); such calculations are very useful for predicting and assigning the corresponding vibrational spectra.

Consideration of the formate ion as an isolated species has on the other hand induced several theoretical investigations. To the best of our knowledge, the most recent one is the work cited,[4] in which $HCOO^-$, NH_4^+, HCOOH, and several hydrated clusters of these species were studied using density functional (DFT) methods. The calculations allowed a discussion on the assignment of the observed spectra. Molecular dynamics methods have also been employed to study some specific properties of the formate ion.[14]

In this investigation, we have pursued a deeper understanding of the structure and spectroscopic properties of the formate ion. We have recorded spectra of liquid solutions of formate salts and also of low-temperature samples obtained after most of the water content had been removed. Using specific theoretical methods for solids, we have modeled the crystals of sodium formate and ammonium formate, and after relaxing the structure, we have predicted their vibrational spectra, which are then compared to the experimental recordings. We have also studied the structure of ionic and neutral species involved in the molecules mentioned above by high-level ab initio methods, followed by the prediction of their anharmonicity-corrected spectra. From the optimized structures, we have conducted a study of the bonding properties of the formate ion, which provides a clear graphical picture of the structural differences found for this ion.

2. Methodology

Experimental Section. We have made use of the hyperquenching experimental technique,[15] which in our case consisted of a rapid expansion of droplets of the appropriate liquid solution into a low-temperature chamber containing a cold substrate, where the droplets immediately freeze, followed by a controlled warming to induce water sublimation. The substrate is then cooled again, leading to the crystalline salts. The whole process is monitored by infrared (IR) spectroscopy, using a Bruker Vertex 70 FTIR spectrometer coupled to the cold chamber. A more thorough description of our experimental setup and procedure is provided in ref 3.

Solutions of HCOONa and $HCOONH_4$ were prepared at room temperature with a 7:100 salt:water ratio. Vacuum expansion and freezing at 14 K, and subsequent warming at 210 K and recooling again at 14 K, were performed as indicated above. Spectra of the corresponding samples at each stage are shown below, with a full description and a subsequent discussion.

Theoretical. We have performed theoretical calculations of two types, specific for solid systems on one hand and for isolated individual molecules and ions on the other. Solid crystals of sodium formate and ammonium formate have been treated using CASTEP,[16] a program specifically designed to deal with several properties of solids, not only geometry optimization and prediction of spectra, as used in this investigation, but also

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dynamics, optical properties, including the density of phonon states, and others. For the geometry optimization, we have selected a set of parameters as follows. For sodium formate, the PBE gradient-corrected (GGA) functional[17] was used with convergence criteria of 2.0×10^{-5} eV/atom, 0.05 eV/Å, 0.002 Å, and 0.1 GPa for the energy, maximum force, maximum displacement, and maximum stress, respectively. Norm-conserving pseudopotentials with a plane wave energy cutoff of 550 eV were also used. The calculations were performed at the Γ point only, after the consistency had been checked over the entire Brillouin zone for these ionic crystals. Ammonium formate required more strict calculations to reach the equilibrium geometry, with values of 1.0×10^{-5} eV/atom, 0.03 eV/Å, 0.001 Å, and 0.03 GPa for the respective parameters as specified above, and 700 eV for the energy cutoff.

We have conducted ab initio calculations of the individual molecules of the salts mentioned above and of related molecules and ions by means of the Gaussian 03 suite.[18] We chose a fairly high level of theory, MP2/aug-cc-pvTZ, which afforded us the ability to undertake the prediction of vibrational spectra with a reasonable level of accuracy. The calculations were performed on the neutral (NaCOOH, NH_4COOH, HCOOH, and NH_3) and ionic ($HCOO^-$ and NH_4^+) forms, because both types of species may be expected to be present in some of the samples experimentally prepared. The different behavior of some vibrations in the two molecular types can be used as an aid in the assignment of the spectra. This level of theory permitted the calculation of the anharmonicity-corrected vibrational spectra, with interesting results as discussed below.

Subsequently, we have analyzed the topological properties of the formate anion in the two salts using the Bader's Atoms in Molecules (AIM) method[19,20] as implemented in the MOR-PHY98 package.[21] We worked also at the MP2/aug-cc-pvTZ level, adequate for the expected accuracy of these results.

3. Results and Discussion

Solids. The initial geometry for the CASTEP calculations was taken from Markila et al.[9] for the sodium crystal and from Nahringbauer[10] for the ammonium compound. The former is a monoclinic crystal, $C2/c$, with four molecules in the unit cell ($a = 6.259$ Å, $b = 6.757$ Å, $c = 6.172$ Å, and $\beta = 116.14°$) and two in a primitive cell, and the latter is also monoclinic but in space group Pc, with two molecules in the unit cell ($a = 3.814$ Å, $b = 4.679$ Å, $c = 9.112$ Å, and $\beta = 91.17°$). Figure 1 shows the optimized structures of the solids, and Table 1 presents a summary of the most important geometrical parameters, both from the original diffraction papers and with the results of this calculation.

The results in Table 1 show that the calculated structures agree reasonably well with the X-ray diffraction measurements. The solid state calculations tend to underestimate the C−O distances and to overestimate the C−H distances, although the difficulty in measuring accurate H atom positions in early X-ray investigations is well-known. The angles, on the other hand, are very precisely reproduced. The N−H···O hydrogen bonds in the ammonium ion vary for the four types within the unit cell, and the values quoted are averages. On the whole, we may assume that the theoretical structure is plausibly accurate and permits the prediction of the spectra. This table collects also the corresponding ab initio calculated values for the isolated molecules, discussed in more detail below.

The recorded spectra of samples at three stages of the experiment are shown in Figures 2 and 3. Water absorptions dominate the spectra of the room-temperature liquid solution
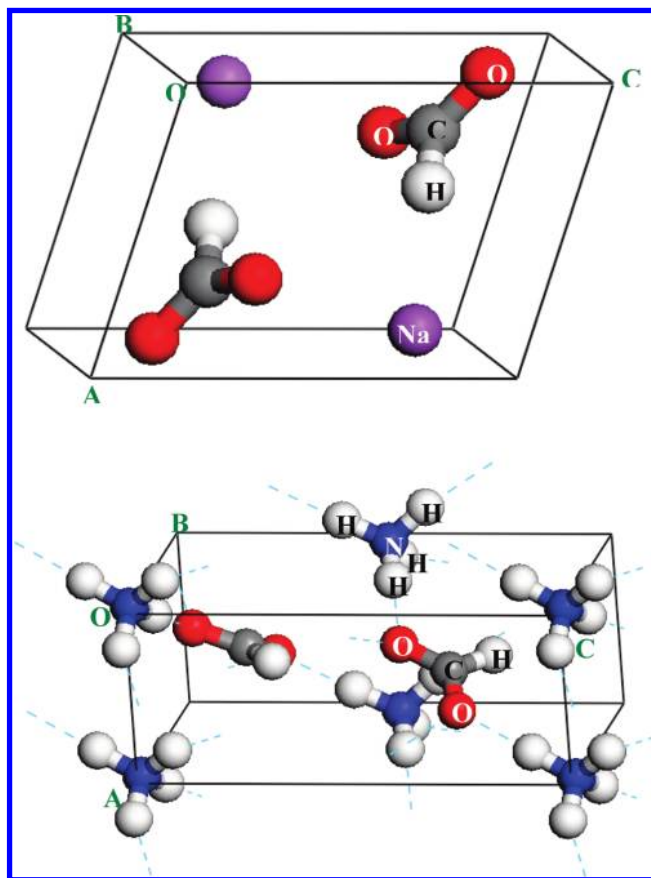

Figure 1. Schematic representation of the calculated crystal structures: (top) NaCOOH (primitive cell) and (bottom) NH_4COOH (unit cell).

TABLE 1: Geometrical Parameters of NaCOOH and NH_4COOH

	NaCOOH			NH_4COOH			
	crystal		isolated	crystal			isolated
	X-ray[a]	this work[b]	this work[c]	X-ray[d]	this work[b]		this work[c]
H−C (Å)	0.99	1.112	1.101	0.903	1.113		1.101
C−O (Å)	1.246	1.177	1.267	1.246, 1.237	1.175, 1.177		1.335, 1.206
O−C−H (deg)	116.9	117.0	117.1		116.8		122.7, 113.4
O−C−O (deg)	126.3	126.0	125.9	126.3	125.9		123.9
N−H···O (deg)				2.845	2.814		2.785

[a] From ref 9. [b] CASTEP.[16] [c] Gaussian,[18] ab initio, MP2/aug-cc-pVTZ. [d] From ref 10.

and of the ice matrix formed by hyperquenching deposition at 14 K (Figure 2, top and bottom, respectively). It is interesting to notice how the stronger formate vibrations, clearly visible in the spectra of the liquid (top), are barely noticeable in the deposited solids at 14 K. The same effect was observed for the strong ammonium band at 1400 cm^{-1} in the spectrum of NH_4Cl samples subjected to a treatment similar that in this work.[3,22] The suggested explanation for this has been laid on the very broad band structure that the formate (or ammonium) vibrations induce as a consequence of the very disordered environment created when amorphous lumps are formed after the impingement of solution droplets on the cold surface in the hyperquenching experiment. Water bands are much stronger and blur the whole region between 2000 and 1200 cm^{-1}. When the samples are heated until water sublimation and cooled again, the environment surrounding the ionic structures becomes more ordered and the spectral features of $HCOO^-$ (and of NH_4^+) stand out strongly, which can be seen in Figure 3. This figure includes
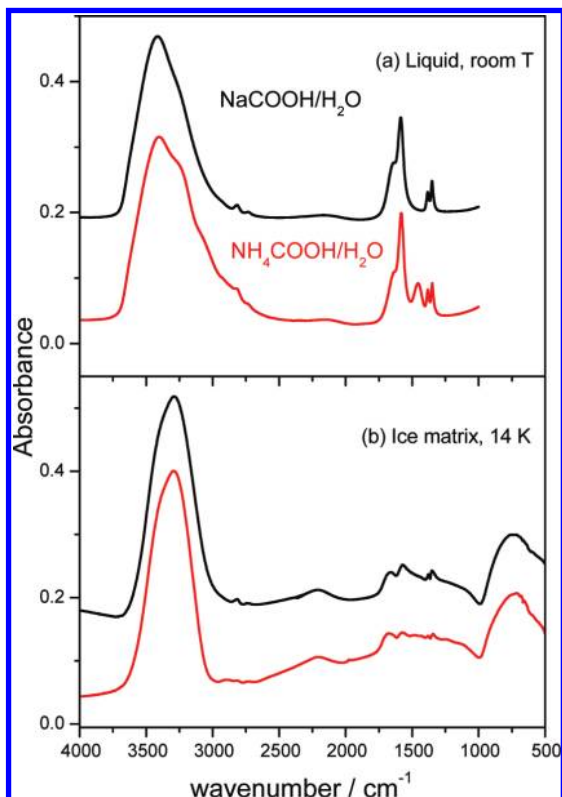
Figure 2. Transmission IR spectra of (a) 7:100 NaCOOH/H$_2$O and NH$_4$COOH/H$_2$O liquid solutions at ambient temperature and (b) 8:100 NaCOOH/H$_2$O (black) and 7:100 NH$_4$COOH/H$_2$O (red) solids deposited by hyperquenching at 14 K. Spectra are offset for the sake of clarity.
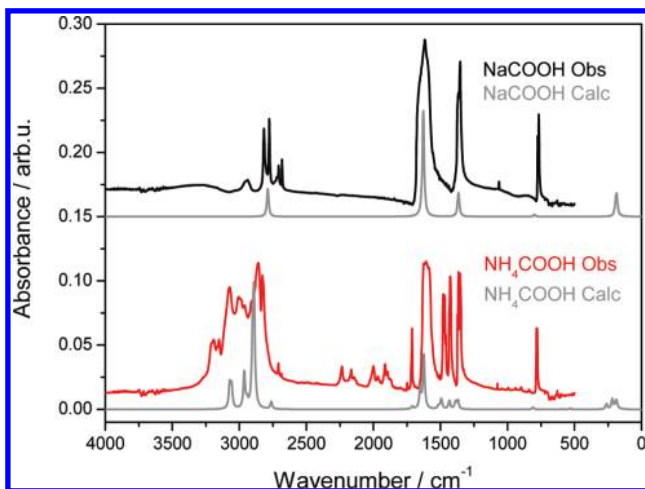

Figure 3. Experimental and simulated IR spectra of NaCOOH (top) and NH$_4$CHOOH (bottom). Experimental samples were salt residues obtained after the samples in Figure 2b had been heated to 210 K and then cooled to 14 K. The absorbance scale in arbitrary units. Spectra are offset for the sake of clarity.

a simulation of the spectra of the crystals, as predicted using CASTEP, where a Lorentzian profile of the constant half-width (8 cm^{-1}) has been used to visualize all vibrations.

We present in Table 2 a summary of the relevant vibrations of the formate ion in the two solids under study, consisting of six normal modes and two overtones observed in the experimental spectra. All vibrations appear as doublets in the crystals, arising from in-phase or out-of-phase combinations of motions of the molecules in the unit cell. The intensity of the lines within each doublet is different, and in fact, one of each pair is missing in the sodium compound, which has C_{2h} local symmetry. All

TABLE 2: Observed and Calculated Spectra in the Mid-IR Region of the Formate Ion in NaCOOH and NH$_4$COOH Crystals[a]

	NaCOOH		NH$_4$COOH	
	observed	calculated	observed	calculated
ν_6	768 (m)	797.6 (0)	777 (m)	808.6 (1.2)
		799.0 (1.1)		809.4 (0.7)
ν_5	1063 (w)	1084.3 (0)	1075 (w)	1096.8 (0.1)
		1088.2 (0)		1097.3 (0)
ν_4	1352 (s)	1363.6 (5.2)	1348 (s)	1369.2 (2.7)
	1365 (s)	1366.9 (6.9)	1353 (s)	1369.6 (5.7)
ν_3		1367.8 (0)	1365 (s)	1386.5 (6.0)
		1369.8 (0)	1371 (s)	1392.4 (1.3)
ν_2	1580–1670 (vs)	1628.1 (51.8)	1580–1624 (vs)	1623.8 (52.6)
		1629.0 (0)		1651.1 (18.5)
$2\nu_3, 2\nu_4$	2680, 2706 (w)		2686, 2708 (w)	
ν_1	2776–2816 (m)	2787.6 (13.6)	2819 (s)	2760.9 (3.3)
		2790.5 (0)	2828 (s)	2763.4 (3.9)

[a] Only the vibrations in which the formate ion is dominant are listed.

"gerade" vibrations from A_g and B_g symmetry species would be forbidden in the infrared spectrum of the pure crystal. The ammonium counterpart has C_s symmetry, and all of its vibrations are allowed. In the compressed spectra shown in Figure 3, it is not easy to observe the splittings in the NH$_4$COOH trace. The experimental spectra correspond most likely to small microcrystals with an uncertain degree of disorder and yield broad bands for most of the vibrations. Besides, the presence of low-concentration residues of the parent molecules, ammonia and formic acid and even water, cannot be discarded. All these facts contribute to the differences found between observed and calculated spectra, but the general agreement in the frequency and relative intensity for the main normal modes of formate can be considered satisfactory.

The strongest formate vibrations are assigned as O–C–O angle bending at ~770 cm^{-1}, C–H bond wagging and C–O bond stretching at 1350–1370 cm^{-1}, another C–O bond stretching involving the strongest C–O bond at ~1600 cm^{-1}, and C–H bond stretching at ~2800 cm^{-1}. A very weak mode at ~1070 cm^{-1} can be attributed to an out-of-plane C–H bond bending.

Isolated Species. The values collected in Table 1 show that the calculated ab initio geometries for the formate moiety in individual sodium formate and ammonium formate molecules are in general terms not very different from those of the crystalline forms. The gas phase structures of isolated species are shown in Figure 4. In the case of the formic acid, there are two well-known conformers (Z and E), although the most stable, Z (trans), is the only one represented. For the NH$_4$COOH molecule in the gas phase, the acidic H atom remains linked to its O, whereas in the solid, two ionic species, HCOO$^-$ and NH$_4^+$, are formed. This feature has been recently analyzed in clusters of water, formic acid, and ammonia.[4] The authors observed that when the number of water molecules is increased (three or more) the formic acid spontaneously transfers the proton and the ionic species (formate and ammonium) are formed.

The refined structures describe real minima in the potential energy surface and can be used to predict the corresponding vibrational spectra. We have conducted such calculations, including anharmonicity corrections, hoping to achieve a better representation of experimental spectra (taken from the literature). Table 3 presents the calculated vibrational frequencies of the formate anion, compared to some observed values and to those of formic acid. We have included for the sake of completeness the corresponding results for the ammonium cation and the
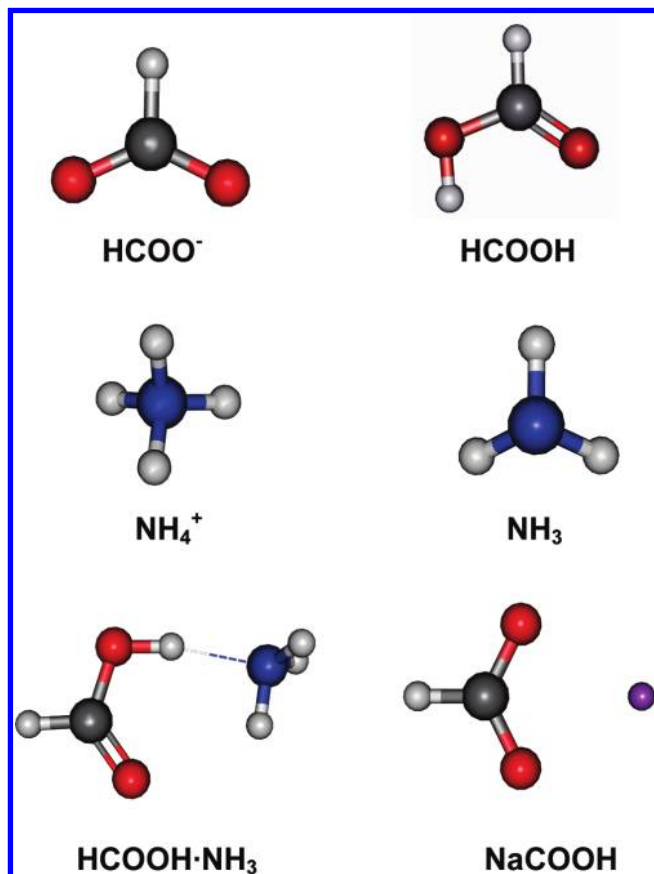
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Figure 4. Schematic representation of the molecular species under study.

ammonia molecule. Some comments can be drawn from the results in the table.

The agreement between observed values and anharmonicity-corrected frequencies is, in general terms, quite good, which confirms the adequacy of the selected level of computation. Frequency differences between the ions and the neutrals can be strikingly large, even though some normal modes could be thought to keep a similar description. For the formate ion, the O–H stretching mode of the acid obviously disappears, but the C–H stretching is red-shifted in the ion by more than 500 cm^{-1}. The strong C–O vibration at 1760 cm^{-1}, ν_3 in the acid, is also red-shifted, but only by $\sim$120 cm^{-1}, and the weak C–H wagging band, ν_4 in HCOOH and ν_6 in HCOO$^-$, by only 50 cm^{-1}. On the other hand, the second C–O vibration, ν_2 in HCOO$^-$, can be related to two lower-frequency mixed modes, ν_5 and ν_6 in the acid, in a manner like that of the ν_3 band of the

TABLE 4: Summary of Bonding Properties

	NaCOOH				NH$_4$COOH		
bond	r	ρ	$\nabla^2\rho$	bond	r	ρ	$\nabla^2\rho$
C–O1	1.267	0.368	−0.468	C–O1	1.216	0.412	−0.252
C–O2	1.267	0.368	−0.468	C–O2	1.327	0.318	−0.505
C–H	1.101	0.290	−1.166	C–H1	1.094	0.298	−1.227
O1–Na	2.270	0.025	0.180	O1–H2	1.006	0.313	−2.292
O2–Na	2.270	0.025	0.180	H2–N	1.732	0.051	0.068
ring point		0.019	0.128	H3–O2	2.425	0.011	0.048
				ring point		0.011	0.043

ion, with two counterparts in the acid, ν_7 and ν_9. Finally, the out-of-plane C–H bending remains practically unshifted, ν_4 in the ion and ν_8 in the acid, being inactive or very weak in the respective spectra. Even more marked effects are found for the ammonia species, where a considerable symmetry change is produced. In tetrahedral NH$_4^+$, the symmetric N–H stretch is forbidden, but the asymmetric ν_3 mode has three components that would correspond to ν_1 and ν_3 (doubly degenerate) of NH$_3$, with a shift of $\sim$120 cm^{-1}. The ammonia inversion (ν_2) does not have a totally equivalent counterpart in NH$_4^+$, and the HNH deformation, the doubly degenerate ν_4 mode in both cases, is shifted by $\sim$180 cm^{-1}.

Topological Analysis. We have conducted a study of the bonding structure of the isolated species. The main features of this analysis are collected in Table 4 and Figure 5. This figure depicts electron density contours for NaCOOH and NH$_4$COOH. Bond critical points (saddle points of the electron density) are marked by a square dot. The formate ion has a basically planar structure in both cases, but in the sodium compound (Figure 5a), the two C–O bonds are equivalent and a four-member ring is formed, with a ring point of minimum density shown by a triangle. The C–O bonds are much stronger than the ionic O–Na bonds, with large electron density ρ and a high negative value of the Laplacian of density $\nabla^2\rho$ in the critical points, which indicates strong charge concentration at those points, whereas the positive values of $\nabla^2\rho$ at the O–Na bonds reveal charge depletion. The O–Na links are quite ionic in nature, as implied by a charge transfer of 0.917 e (not shown in Table 4).

As for ammonium formate, the C–O bonds are no longer equivalent but have fairly different characteristics. Although both are still strong bonds, the C–O1 bond is weaker and longer than the C–O2 bond. The O1···H2···N structure forms a typical H-bond liaison, all three atoms lying in an almost straight line with a total O–N distance of 2.72 Å, and very small charge transfer, a large charge density concentration close to the H, and charge depletion along the H–N direction. A weak interaction (see the ρ value in Table 4) is seen to occur between H3 and O2, which also implies the formation of a ring critical

TABLE 3: Calculated and Experimental IR Frequencies of Isolated Species[a]

	HCOOH			HCOO$^-$			NH$_3$			NH$_4^+$	
	MP2[b]	exptl[c]		MP2	exptl[d]		MP2	exptl[c]		MP2	exptl[d]
ν_7	619.4 (41)	625	ν_3	731.9 (17)	730	ν_2	959.0 (139)	931/968	ν_4	1440.7 (140)	1447
ν_9	623.3 (134)	642	ν_4	1024.9 (0)		ν_4	1621.0 (14)	1627	ν_2	1692.3 (0)	
ν_8	1036.7 (4)	1033	ν_2	1308.7 (97)	1323	ν_1	3360.2 (3)	3336	ν_1	3237.1 (0)	
ν_6	1097.4 (264)	1105	ν_6	1341.4 (5)		ν_3	3483.9 (8)	3443	ν_3	3358.2 (194)	3343
ν_5	1263.3 (16)	1223	ν_5	1621.2 (880)	1629						
ν_4	1389.7 (1)	1380	ν_1	2463.4 (483)	2456						
ν_3	1760.6 (332)	1776									
ν_2	2959.8 (31)	2944									
ν_1	3557.7 (79)	3570									

[a] All MP2 results obtained in this work. Frequencies in cm^{-1}, intensities (in parentheses) in km^{-1} mol^{-1}. [b] From this work, MP2/aug-cc-pVTZ. [c] From ref 23. [d] From ref 24.
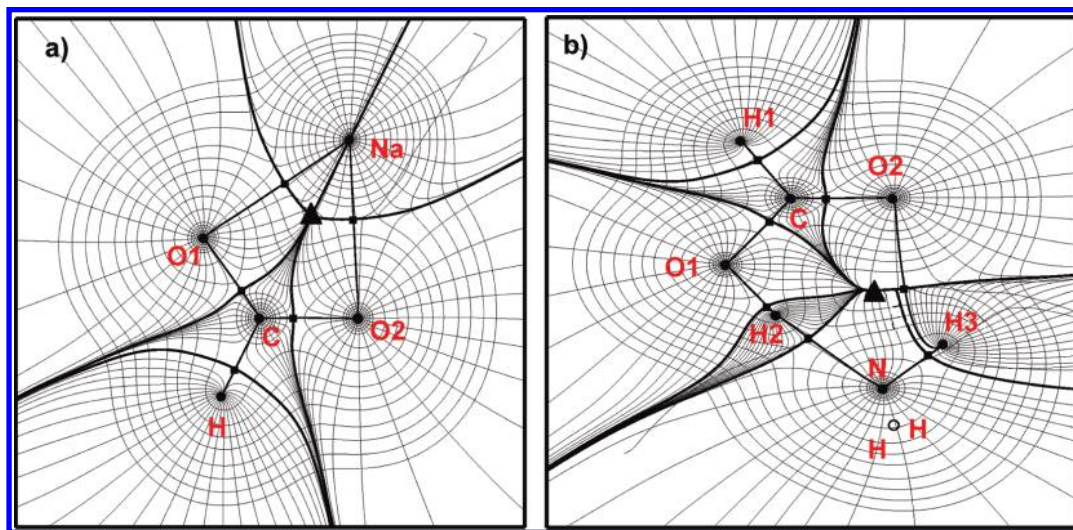
Figure 5. Superposition of the gradient vector field of ρ and contour map of the electron density for NaCOOH (a) and NH$_4$COOH (b).

point. The results for this molecule, studied as an isolated species, reveal that ammonia on one side and formic acid on the other are the prevailing systems, weakly bound to each other, in clear contraposition to the ionic structure seen in the crystal.

4. Conclusions

This paper presents a study of the formate ion, based on experimental and theoretical evidence. The experimental results consist of IR spectra of samples of sodium formate and ammonium formate under different conditions, namely, liquid water solutions, ice matrices formed by hyperquenching expansions of the solutions, and ionic salts prepared by water sublimation of the matrices and further cooling. The theoretical part is focused along two lines. On one side, using a solid state-oriented program, the ionic crystals of those species are modeled and their vibrational properties are predicted, to be compared to the observed spectra; on the other side, the individual molecules and the corresponding ionic species are studied by ab initio methods, with the main objective being to provide a comprehensive body of information and to allow a topological analysis to be conducted. The conclusions drawn from this investigation are summarized below.

The experimental technique employed is a very powerful tool for studying frozen ionic systems freed from interaction with water. The presence of hidden infrared bands of the ions revealed during the annealing process is striking. The calculations of the solid crystals of NaCOOH and NH$_4$COOH using CASTEP reproduce adequately the X-ray diffraction data and lead to the prediction of IR spectra that compare well with the experimental spectra and permit a thorough assignment of the observed features.

The quality of the ab initio calculations for individual systems is reflected by the good reproducibility of their observed spectral characteristics. These calculations provide the ground for a topological analysis of the formate species indicated above, performed using the Atoms In Molecules methodology. This analysis shows the very different characteristics that the HCOO moiety adopts in the two systems studied. The formate ion appears to have a high degree of plasticity that allows adoption of fairly different structures depending on the cation to which it is linked. In the gas phase, the ammonium formate molecule shows a structure in which neutral species, ammonia and formic acid, are linked by a H-bond. In the solid phase, a proton transfer

occurs and ionic species are formed. On the other hand, sodium formate yields ionic species both in the gas phase and in the solid phase.

Infrared spectroscopy and solid state and ab initio calculations provide appropriate tools for investigating this system.

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