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Structural transformation in formic acid on ultra cold ice surfaces

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Abstract

We have investigated the effect of ice substrate on the temperature dependent structural changes of formic acid. Infrared spectra of HCOOH@KBr , $\text{HCOOH@H}_2\text{O}_{\text{amorphous}}$ and $\text{HCOOH@H}_2\text{O}_{\text{crystalline}}$ were measured in the temperature range of 18–180 K (X@Y represents X deposited on Y). At 18 K formic acid deposited over ice exists principally as its dimer. Upon increase of temperature, the dimer gets converted to the polymeric crystalline form. In the case of amorphous ice surface, this conversion starts at a lower temperature of 37 K. For KBr and crystalline ice surfaces, this occurs at 98 and 83 K, respectively. The dangling –OH found on amorphous ice surfaces disappears completely upon formic acid deposition. The greater mobility of formic acid molecules on amorphous ice aids in the early onset of its crystallization.

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1. Introduction

Even though, ice is one of the prevalent condensed phases present in the earth's atmosphere, there still remains a gap in our understanding of how atmospheric trace gases interact with ice surfaces. A large number of studies have been performed with HNO_3 and HCl which indicate that a very strong interaction occurs on ice surfaces [1–3]. Studies of organic molecules on ice surfaces are also relevant because the chemistry of adsorbed organic molecules may differ substantially from that of the gas phase. Recent experimental studies have focused on the interaction of *n*-alcohols, acetone and acetaldehyde with ice at tropospheric temperatures [4]. Adsorption behavior of molecules such as acetic acid and hexanal have also been investigated [5]. The phase of ice may affect the adsorption rate, reactivity and structure of the adsorbate. For example, it has been found that uptake of HCl onto atmospheric ice is more rapid than onto crystalline ice [6].

Formic acid is the simplest in the series of carboxylic acids. It is of considerable relevance both from an atmospheric viewpoint and in the context of investigation of amino acids, for which it is a model compound. The presence of oxygenated hydrocarbons in the upper troposphere affects its chemistry due to the formation of HO_x radicals from the former [4,5]. These radicals are responsible for most of the chemical reactions in the upper tropospheric region of the atmosphere. Formic acid can photolytically fragment in the atmosphere forming COOH^\cdot and H^\cdot . These radicals act as sinks for the hydroxyl radical and also help in driving other reactions with the addition of hydroperoxy radicals to the atmosphere. It is important to understand how clouds, which are composed of liquid droplets or ice particles, can participate in the uptake of formic acid as a function of temperature. Recent study of the relative concentration of formic acid and acetic acid in convective air masses towards Greenland and their incorporation into icy crystals reveal that an enhanced ratio of formate (HCOO^-) over acetate (CH_3COO^-) exists in snow [7]. From concentration analysis of ice samples it was found that formic acid was mainly present in its ionized form, while acetic acid existed in its molecular form.

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In space, formic acid is of great interest because it shares similar structural features with the common interstellar molecule, methyl formate and the biologically important molecules such as acetic acid and glycine.

The structure of gaseous formic acid has been studied thoroughly by microwave spectroscopy and electron diffraction [8,9]. Vibrational spectrum of formic acid in the gas phase has been measured by infrared [10–12] and Raman spectroscopies [13]. Solid state low temperature infrared studies by the matrix-isolation technique have been reported [14–16]. There are a number of theoretical investigations on formic acid monomer, dimer and diformate anions as well as on the association of formic acid monomer with other molecules such as CO_2 and ethane [17–20]. Molecular dynamics studies of formic acid in/on ice mostly at tropospherically relevant temperatures have been reported [7].

In the present Letter, we probe the effect of the nature of ice on the structure of formic acid deposited over it. We investigate the nature of the structural transition in formic acid in the temperature range of 18–180 K. In earlier studies we have established desorption behavior of different gases from ice surfaces [21]. The present Letter demonstrates the existence of formic acid dimer in the solid state. Apart from the matrix-isolation studies dimeric formic acid has not been reported in the solid state [14].

2. Experimental

A KBr disc, directly attached to the cold finger of a closed cycle helium refrigerator of Leybolds, was used as the substrate in our experiments. The cryostat was pumped with the help of a turbomolecular pump backed by a double stage rotary pump. The experiments were carried out at a constant base pressure of 10^{-6} mbar. The temperature was measured directly at the sample holder with a platinum resistance thermometer and a copper-constantan thermocouple simultaneously. The infrared spectra were collected in the $4000\text{--}400\text{ cm}^{-1}$ region by a Perkin-Elmer Spectrum One Fourier-transform infrared (FT-IR) spectrometer, with a spectral resolution of 4 cm^{-1} . The sample compartment of the spectrometer was suitably modified for accommodating the cryostat head. The vapors of water and formic acid were deposited on the pre-cooled KBr disc. The formic acid and water used were of high purity and were subjected to freeze-pump-thaw cycles at least three times to remove the dissolved gases. Formic acid (purity 99.5%) was obtained from SRL Pvt. Ltd., India. It was kept in a glass bulb and through a stainless steel tube it was connected to the cryostat at a position directly opposite to the KBr disk. Vapor was deposited either on the solid ice film prepared earlier or on the KBr disc, at 18 K in both the cases. While water vapor

deposited at 18 K produced amorphous ice, the crystalline ice was prepared by warming the ice to 140 K and holding at that temperature for 10 min. The ice was cooled back to 18 K for deposition of formic acid to produce formic acid@ $\text{H}_2\text{O}_{\text{crystalline}}$. Film thickness was not measured directly and deposition was made such that the transmittance reduced by a further 50% for the maximum intense peak. After deposition infrared spectra were collected every 5 K interval up to 300 K.

3. Results and discussion

In gas and liquid phases formic acid exists in the dimer form due to strong hydrogen bonding. The exceptional strength of hydrogen bonding is explained on the basis of the large contribution of the ionic resonance structure. Spectra of the dimeric acids have been studied previously [17]. Formic acid dimer displays intense O–H stretching features in the region of $3100\text{--}2500\text{ cm}^{-1}$. The band is usually centered near 3000 cm^{-1} . Because of strong hydrogen bonding, the free hydroxyl stretching vibration (near 3570 cm^{-1}) due to the monomer is observed only for high temperature vapors. The weaker C–H stretching bands are seen superimposed over the broad O–H band. Fine structure observed on the lower wavenumber side of the broad O–H band represents overtones and combinations of the fundamental bands. Fig. 1 shows the spectra of formic acid in the liquid phase and solid phases.

As the acid was deposited from the vapor phase, the gas phase constituents are deposited as such. Previous reports suggested crystalline structure of formic acid in the temperature range of 77–140 K [11]. The peak assignments have been done using Refs. [11] and [17]. The liquid spectrum assignments are as follows: ca.

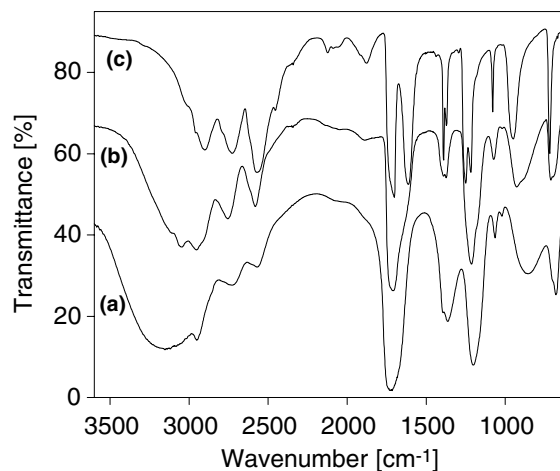


Fig. 1. Infrared spectrum of HCOOH in different forms: (a) liquid HCOOH at 300 K; (b) HCOOH@KBr at 18 K; (c) HCOOH@KBr at 175 K.

3153 cm^{-1} (νOH), 2953 cm^{-1} (νCH), 2726 and 2569 cm^{-1} (νOH), 1725 cm^{-1} ($\nu\text{C}=\text{O}$), 1396 cm^{-1} ($\delta\text{C}-\text{O}-\text{H}$), 1362 cm^{-1} ($\delta\text{H}-\text{C}-\text{O}$), 1202 cm^{-1} ($\delta\text{C}-\text{O}$), 1064 cm^{-1} (δCH), 856 cm^{-1} (δOH) and 700 cm^{-1} (δOCO). Features of the acid spectrum at 18 K over KBr and that of the bulk liquid are similar even though the frequencies are slightly shifted. In the solid form of the acid (Fig. 1b) the bands appear at ca. 3115 cm^{-1} (νOH), 2953 cm^{-1} (νCH), 1890 cm^{-1} ($2\delta\text{OH}$), 1708 cm^{-1} ($\nu\text{C}=\text{O}$), 1389 cm^{-1} ($\delta\text{C}-\text{O}-\text{H}$), 1373 cm^{-1} ($\delta\text{H}-\text{C}-\text{O}$), 1213 cm^{-1} ($\delta\text{C}-\text{O}$), 1072 cm^{-1} (δCH), 927 cm^{-1} (δOH) and 711 cm^{-1} (δOCO). These features match with the dimer features in the literature [11,17]. The values have been shifted slightly to the lower wavenumber region due to molecular interaction. This suggests that in the solid state the deposited molecules exist principally in the dimer form. At higher temperatures (>98 K), bands due to $\text{C}=\text{O}$ and $\text{C}-\text{O}$ split into two strong components. This crystal splitting is seen at 1702 and 1614 cm^{-1} and at 1250 and 1217 cm^{-1} . The crystalline state spectrum occurs at higher temperature and is given in Fig. 1c.

Although, the 18 K spectrum obtained by the deposition of formic acid vapor has the features of the dimer molecules, there are also features corresponding to the crystalline state (Fig. 2a). The $\text{O}-\text{H}$ stretching frequency due to formic acid appears at 3115 cm^{-1} along with a strong peak at 3045 cm^{-1} . The 3045 cm^{-1} peak is due to the crystalline component of formic acid. The three peaks at 3045, 2755 and 2581 cm^{-1} are assigned as due to the three crystal-split components of the $\text{O}-\text{H}$ stretching fundamental [11] (see Fig. 2). The $\text{C}=\text{O}$ stretching (1708 cm^{-1}) and $\text{C}-\text{O}$ stretching (1213 cm^{-1}) frequencies of formic acid dimer are slightly lower than the literature values. This may be due to the existence of dimer molecules as aggregated species. In the

light of these observations we can conclude that at 18 K the acid molecules exist in the form of dimer along with smaller fraction of the crystalline phase.

As the temperature increases, the fraction of the crystalline phase increases. At 98 K a large percentage of molecules have come to the crystalline form and at 135 K the sample turns totally to the crystalline state. This is shown in Fig. 2c,d, respectively. These changes are quite visible from the splitting of the $\text{C}=\text{O}$ stretching peak at 1708 cm^{-1} to 1702 and 1614 cm^{-1} . The $\text{C}-\text{O}$ stretching band at 1213 cm^{-1} is also split into two peaks at 1250 and 1217 cm^{-1} . At higher temperatures all the peaks in the fingerprint region become sharper due to the crystalline nature of the sample. After this till the desorption temperature no phase change is observed (Fig. 2e). At 185 K formic acid is completely desorbed from the KBr disc and the clean KBr spectrum confirms (Fig. 2f) that there was no contamination on the substrate.

Next, we investigated the effect of the nature of ice substrate on the temperature dependent transition of formic acid. Depending on the deposition conditions two forms of ice can be easily prepared [22]. The spectra of formic acid deposited on amorphous ice and crystalline ice are given in Fig. 3. It is found that there is no change in the features of ice due to the deposition of the acid. Comparing the spectra of formic acid on the three substrates, namely KBr, amorphous ice and crystalline ice, we conclude that the nature of the material is unaffected by the substrate. However, the structural transformation of the deposited molecules is highly sensitive to the nature of the ice surface.

As discussed, the dimer \rightarrow crystalline state conversion starts at 98 K in the case of the KBr substrate. Figs. 4 and 5 show the temperature dependent infrared spectra of HCOOH deposited on amorphous ice and crystalline ice, respectively. It is interesting to note that in the case of amorphous ice surface, this conversion starts at 37 K. The whole sample is transferred into the crystalline state within a narrow temperature window of 4 K (Fig. 4). For crystalline ice surface, this change starts at a fairly high temperature of 83 K (Fig. 5) and the conversion is complete at 128 K. This difference can be attributed to the availability of free OH groups in the case of amorphous ice surface. Moreover, the surface of amorphous ice is likely to be irregular so that formic acid can form islands on this surface. But the crystalline ice is hexagonally packed and surface defects are insignificant when compared to amorphous ice. The $\text{C}=\text{O}$ bands do not show substantial shift in position with different substrates suggesting that there is no significant difference in the adsorption chemistry. But, with increase in temperature distinct changes in the OH stretching and bending frequencies are observed. A summary of changes in the OH features of formic acid is given in Table 1. From this it is clear that at 18 K all the features occur at the

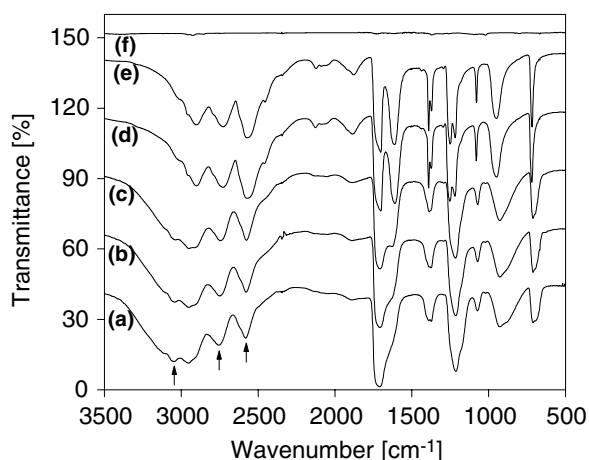


Fig. 2. Infrared spectra of $\text{HCOOH}@KBr$ at various temperatures: (a) 20 K; (b) 60 K; (c) 98 K; (d) 135 K; (e) 175 K; (f) 185 K. Arrows show the OH features due to the crystalline form. The spectra have been offset for clarity.

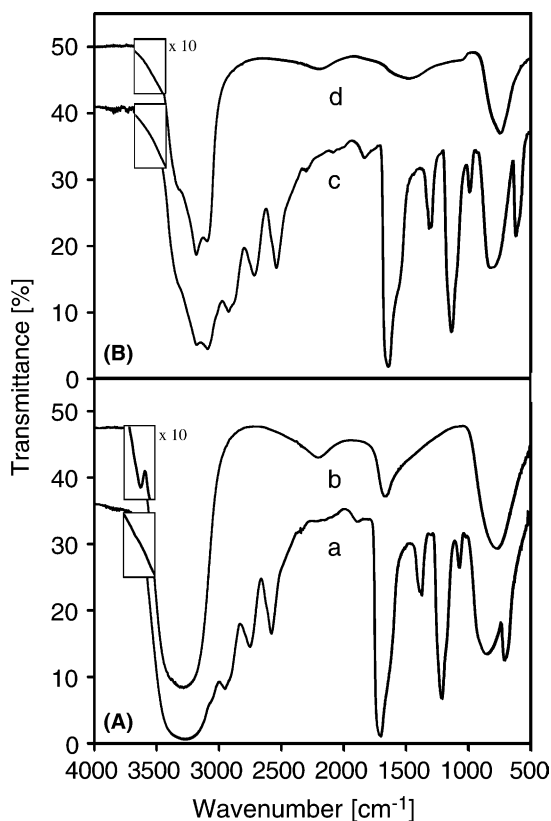


Fig. 3. Infrared spectra of HCOOH deposited on (A) amorphous ice and (B) crystalline ice: (a) HCOOH@H₂O_{amorphous}; (b) H₂O_{amorphous}; (c) HCOOH@H₂O_{crystalline}; (d) H₂O_{crystalline}. Enlarged area in (A) is the region, where H₂O_{amorphous} shows the dangling OH feature. It is clear from (a) and (b) that H₂O_{amorphous} does not have the dangling OH peak in the presence of formic acid. H₂O_{crystalline} (B) does not show the dangling –OH feature as expected. The spectra have been offset for clarity.

same frequency. The temperature of the peak shift is affected by the nature and the type of the substrate. In the case of amorphous ice at ~40 K, OH features of formic acid are red shifted by ~30 cm⁻¹. At this stage (41 K),

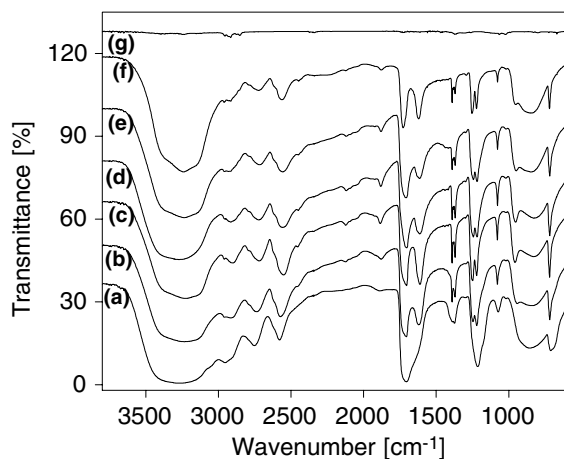


Fig. 4. Temperature dependent infrared spectra of HCOOH@H₂O_{amorphous}: (a) 20 K; (b) 37 K; (c) 40 K; (d) 100 K; (e) 150 K; (f) 175 K; (g) 185 K. The spectra have been offset for clarity.

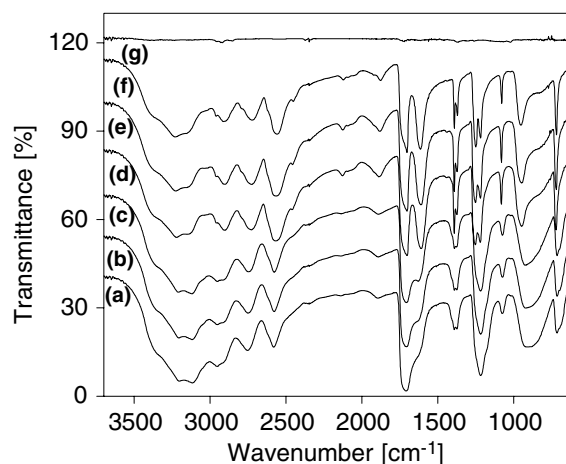


Fig. 5. Temperature dependent infrared spectra of HCOOH@H₂O_{crystalline}: (a) 20 K; (b) 50 K; (c) 83 K; (d) 128 K; (e) 150 K; (f) 175 K; (g) 185 K. The spectra have been offset for clarity.

the entire formic acid is completely converted to the crystalline state. In the case with other two substrates, KBr and crystalline ice, during the conversion (135 and 128 K), these features are shifted by ~30 cm⁻¹. This clearly indicates that the nature of ice affects the hydrogen bonding interaction and hence the dimer-crystalline state conversion also. It is important to note that the HCOOH deposited on amorphous ice does not have any signature of dangling OH band near 3650 cm⁻¹ (see Fig. 3a). Obviously, the surface OH groups have been affected by the deposited formic acid.

Conversion to crystalline state is followed by monitoring the OH bending and O=C=O bending frequencies of formic acid. The OH bending peak of formic acid at ~920 cm⁻¹ and the O=C=O feature at 710 cm⁻¹ are blue shifted by ~25 and ~10 cm⁻¹, respectively, during this change. It is clear that ordered arrangement in the crystalline state affects bending frequencies of OH and O=C=O. To check the reversibility of these processes, the sample was cooled back from 150 K, i.e., after complete crystallization, to 18 K. It is found that dimer-crystalline conversion is irreversible in all cases, viz. KBr, amorphous ice and crystalline ice.

In the case of amorphous ice surface the crystallization starts at 37 K and is complete at 40 K. For crystalline ice surface the values are 83 and 128 K, respectively and in the case of KBr disc the values are 98 and 135 K, respectively. The most prominent observations of chain type crystal structure that we have discussed are the splitting of the C=O vibration at 1702 and 1614 cm⁻¹ and the C–O vibration at 1250 and 1217 cm⁻¹. The large splitting of the carbonyl features may be understood in terms of the electronic structure of the carboxyl unit. Changes in the C–O distances will tend to shift the π electron density, or in other terms, the fraction of double bond character of each C–O bond [11]. The two C–O stretching vibrations of each monomer unit in this case

Table 1
Comparison of OH and O=C=O features of formic acid for three different substrates

	Temperature (K)	OH stretching (cm ⁻¹)		OH bending (cm ⁻¹)	O=C=O bending (cm ⁻¹)
HCOOH@KBr	18	2755	2581	927	711
	40	2750	2579	927	710
	145	2727	2570	948	719
	175	2726	2570	949	718
HCOOH@H ₂ O _{amorphous}	18	2752	2579	923	711
	40	2718	2550	928	718
	145	2717	2558	950	717
	175	2723	2561	950	719
HCOOH@H ₂ O _{crystalline}	18	2751	2580	915	715
	40	2750	2578	917	712
	145	2726	2565	945	718
	175	2723	2557	951	717

are strongly coupled into symmetric and antisymmetric stretching modes. If the successive monomer units vibrate in-phase the frequency will be ~ 1600 cm⁻¹. If the vibrations are out-of-phase, the coupled vibration will occur at a higher frequency of about 1700 cm⁻¹.

In summary, we have investigated the structural transformation of formic acid. At low temperature, formic acid vapors can be deposited in the dimer form. In the solid state at 18 K, formic acid exists as a mixture composed of the dimeric and crystalline forms. At higher temperature, the whole sample is converted to an ordered polymeric crystalline state. The temperature of this structural transformation varies with the nature of the substrate. In the case of amorphous ice surface this conversion starts at a lower temperature of 37 K. For KBr and crystalline ice surfaces, it occurs at 98 and 83 K, respectively. It appears that the early onset of crystallization in amorphous ice is due to the greater mobility of the water molecules on the surface which could promote crystallization of the formic acid layers above. A dangling OH bond mediation is likely as these bonds are not observed after formic acid deposition. It is important to note that formic acid crystallization does not lead to crystallization in ice.

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