Interactions of Oxalic Acid and Ice on Cu Surface

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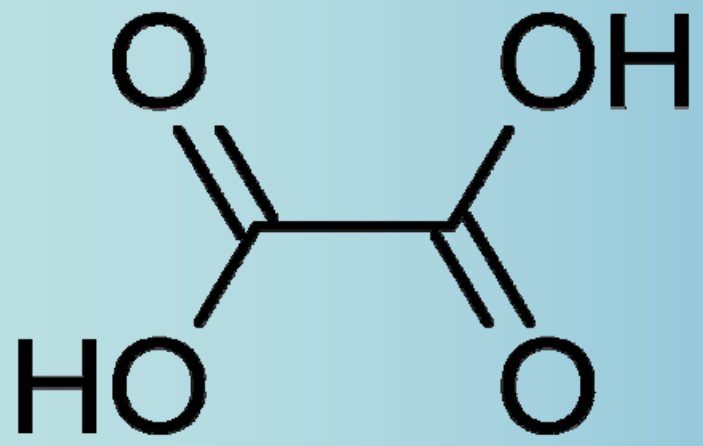

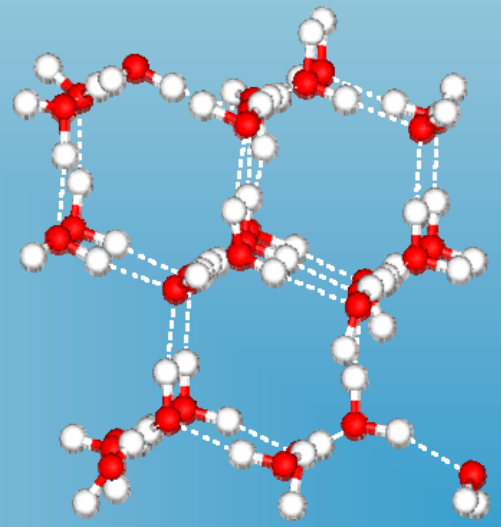

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Introduction

- Dicarboxylic acid components are approximately 30-50% of the total organic particulate matter in troposphere
- Oxalic acid ($C_2H_2O_4$) comprises 37-69% of the total dicarboxylic acids
- Oxalic acid and its oxalate enhances photochemical hydrogen peroxide production
- Hydrogen peroxide is responsible for the oxidation of many tropospheric species
- The hydration or deprotonation of $C_2H_2O_4$ near the ice surface is an important issue to elucidate the nature of the heterogeneous reaction between $C_2H_2O_4$ and bromine on ice surfaces

Experimental techniques

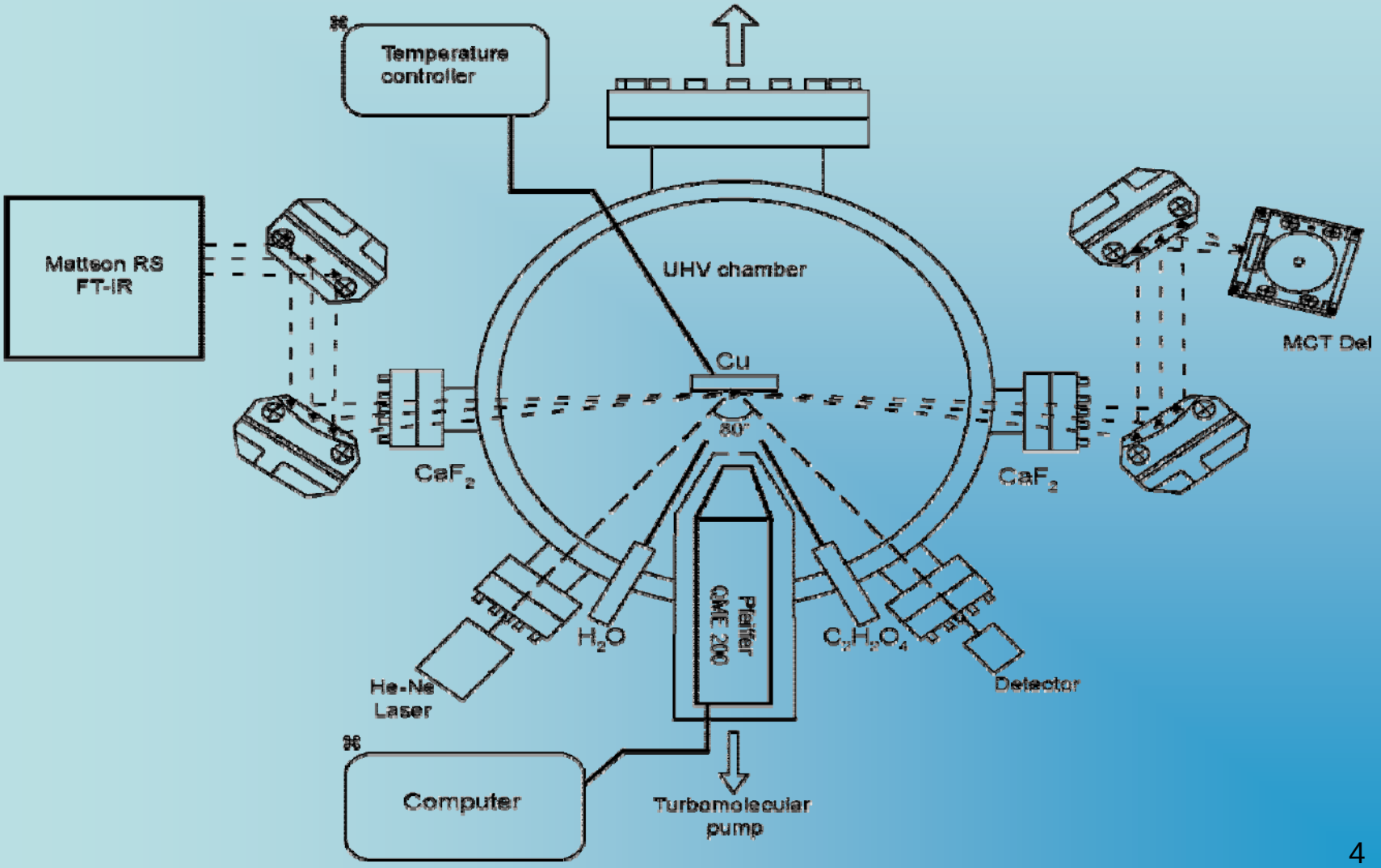
RAIRS (reflection absorption infrared spectroscopy)

TPD (Temperature Programmed Desorption)

various kind of samples

- Adsorption of H_2O on $C_2H_2O_4$ covered Cu surfaces ($H_2O/C_2H_2O_4/Cu$)
- Adsorption of C2H2O4 onH_2Ocovered Cu surfaces ($C_2H_2O4/H_2O/Cu$)
- Co-adsorption of H_2O and $C_2H_2O_4$ on the Cu surface ($C_2H_2O_4+H_2O/Cu$)

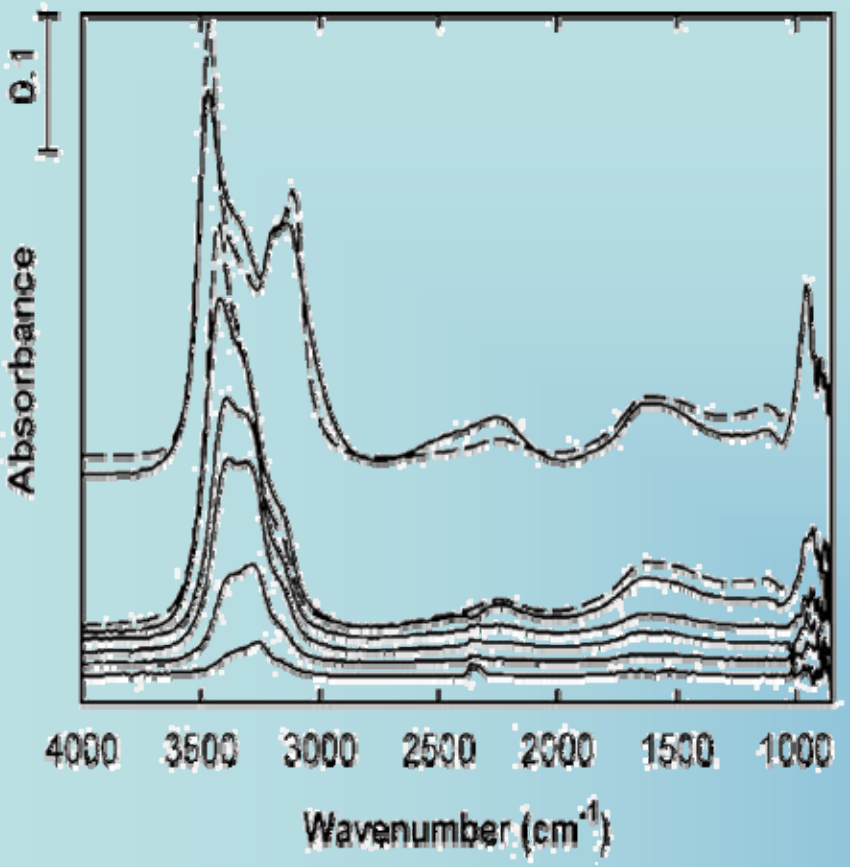
Schematic of the RAIRS-QMS apparatus.



Ice-Film Thickness
The optical interference technique

- A 632.8 nm He-Ne laser beam was incident on the ice-covered Cu surface at 40° from the surface normal
- The laser beam was reflected at both the vacuum-ice and the ice-Cu interfaces
- An interference pattern was observed due to the difference in the optical path length of the two reflected beams
- The thickness d of the ice film at the constructive interference fringes was calculated
- IR absorbance of the OH bands are used to determine the thickness of the ice film for d <140 nm
- The integrated RAIR absorbance is proportional to the thickness of thin ice

$$d = \frac{m\lambda \cos\theta_2}{2n_1 \sin\theta_1 \sin\theta_2 - 2n_2}$$



RAIR spectra of ice films of various thickness depicted at 155 K

The ice-film thickness was 13, 30, 100, 120, 200, and 700 nm, from the lower to the upper solid-line plot

❖2800 to 3700 cm-1 shows OH stretching modes (v_1 and v_3)

❖The band at ~3100 cm^{-1} is due to reflection of s-radiation and the increased absorption of p-radiation

❖The band at ~ 2250 cm^{-1} is attributed either to a combination of the bending mode of $H_2O(v_2)$ with the hindered rotational lattice mode (v_R) or to the third overtone of the hindered rotational lattice mode ($3v_R$)

❖band at ~ 1640 cm^{-1} is attributed to the ice bending mode (v_2)

❖OH dangling band at ~3700 cm^{-1}(ASW) is not observed suggesting that the ice film on the Cu surface is polycrystalline

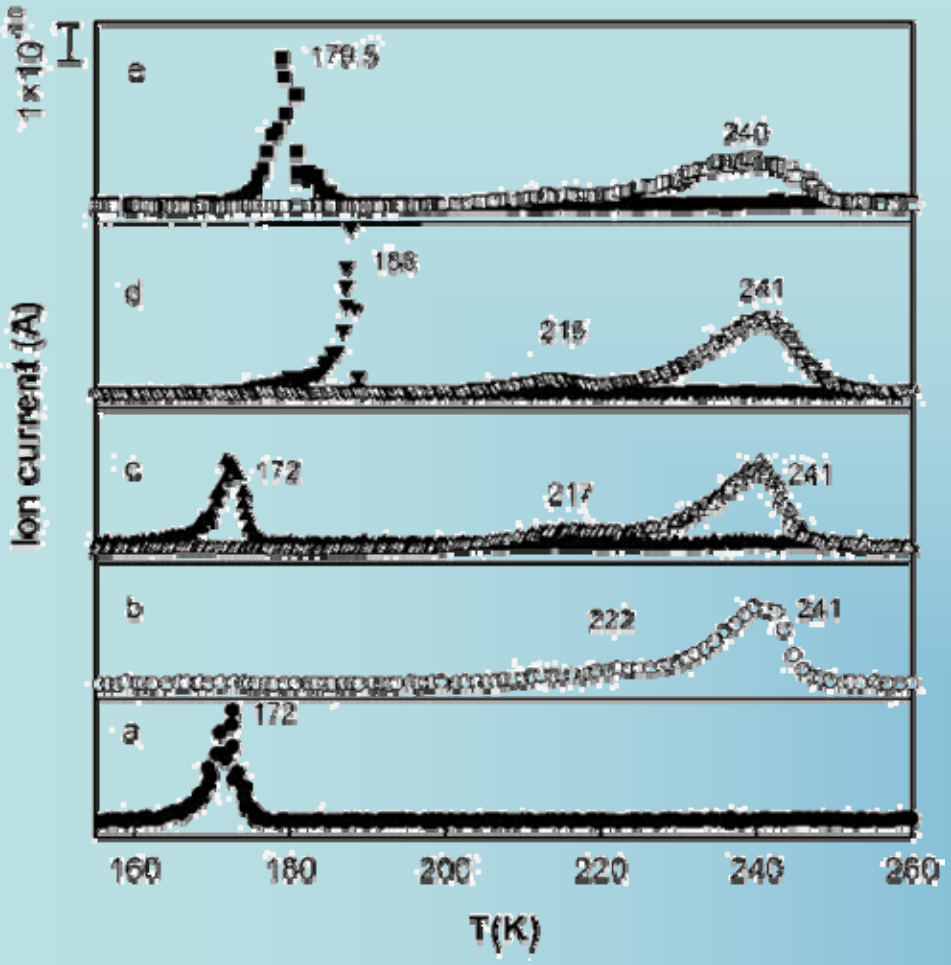


Fig 3: TPD spectra for ice and $C_2H_2O_4$ on the Cu surface

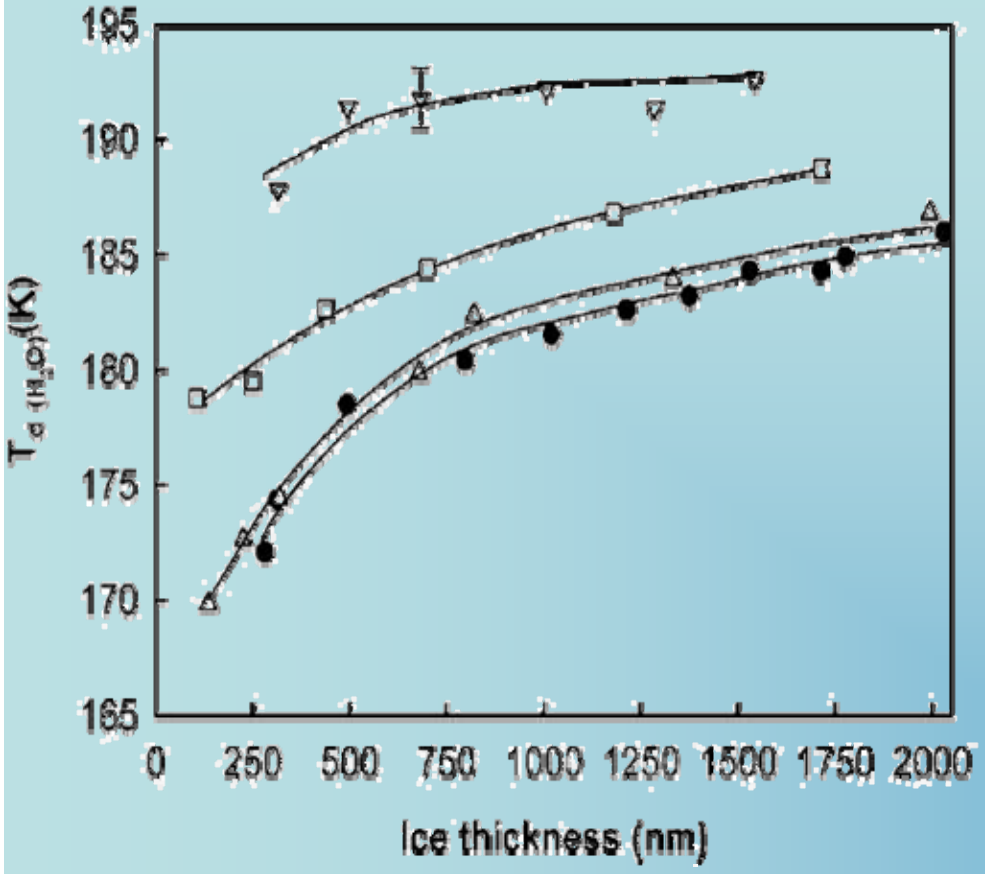
(a)TPD spectrum of 210 nm ice on the Cu surface

(b) TPD spectrum of 5.7 L $C_2H_2O_4$ on the Cu surface

(c) TPD spectrum for 205 nm ice on the 5.8 L $C_2H_2O_4$ covered Cu surface

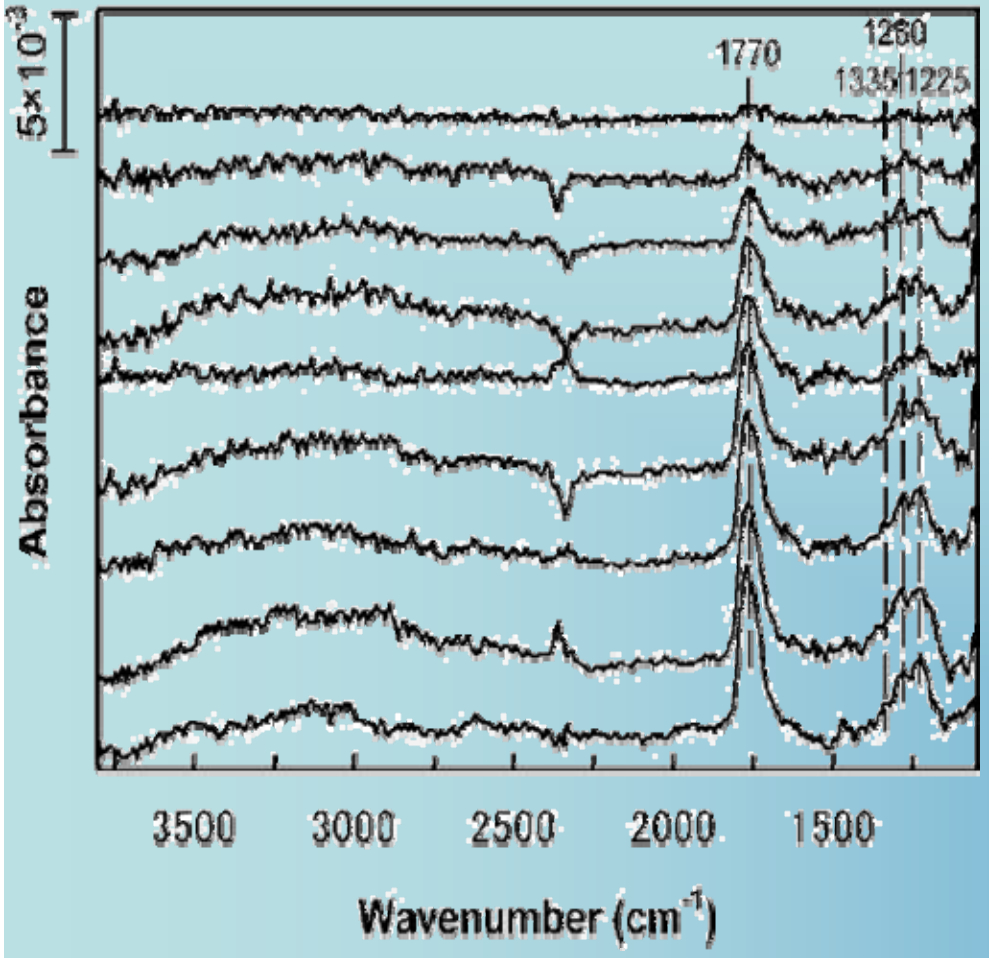
(d) TPD spectrum of 6.2 L $C_2H_2O_4$ over the 215 nm ice covered Cu surface

(e) TPD spectrum of codeposited 220 nm ice and 5.5 L $C_2H_2O_4$ on the Cu surface



Ice desorption temperature T_d as a function of the film thickness
H_2O/Cu
$H_2O/C_2H_2O_4/Cu$
C2H2O4+H2O/Cu and
$C_2H_2O_4/H_2O/Cu$ (see from bottom to top)

- The desorption temperature (T_d) of ice increases with the thickness of the ice film
- Thermal energy is required to break the H-bonding interactions in ice and ice-surface interactions leads to desorption of H_2O from the surface
- As thickness increases H_2O-H_2O attractive interactions (H-bonds) are available, and the total lateral interaction energy is higher hence more thermal energy is required
- H_2O desorption temperature for $H_2O/C_2H_2O_4/Cu$ is nearly identical to that forH_2O/Cu
- The interaction between H_2O molecules is weaker than that between $C_2H_2O_4$ molecules
- $C_2H_2O_4$ molecules do not desorb along with H_2O at the ice T_d



Adsorption of $C_2H_2O_4$ on the Cu surface at 155 K for varying coverages 0.5, 1.4, 2.0, 3.4, 4.0, 5.2, 6.2, 6.6, and 7.4 L from top to bottom

- Band at 1770 cm^{-1} is attributed to the carboxylic stretching mode $\nu_{C=O}$
- Bands at 1335, 1280, and 1225 cm^{-1} are associated with two coupled modes, the δ_{COH} and ν_{C-O} modes
- A broad OH stretching band is observed in the range of 2780-3450 cm^{-1} and peaking at approximately 3100 cm^{-1}
- Intra- or inter hydrogen bonds among $C_2H_2O_4$ molecules in the same layer or from the neighboring layers are seen
- At higher coverage the $C_2H_2O_4$ molecules get H-bonded to each other with different structures as well as surface bonded $C_2H_2O_4$
- Neither hydrogen oxalate nor oxalate formed on the Cu surface at 155 K
- The adsorbed $C_2H_2O_4$ is in its molecular state

Desorption of $C_2H_2O_4$ from the Cu Surface

- $C_2H_2O_4$ adsorbs on the Cu surface in two adsorption states when it is deposited on the surface at 155 K (fig 3-b)
- The T_d for sII-$C_2H_2O_4$ (241 K) increases with increasing $C_2H_2O_4$ coverage
- The T_d for sI-$C_2H_2O_4$ is unaffected by the $C_2H_2O_4$ coverage

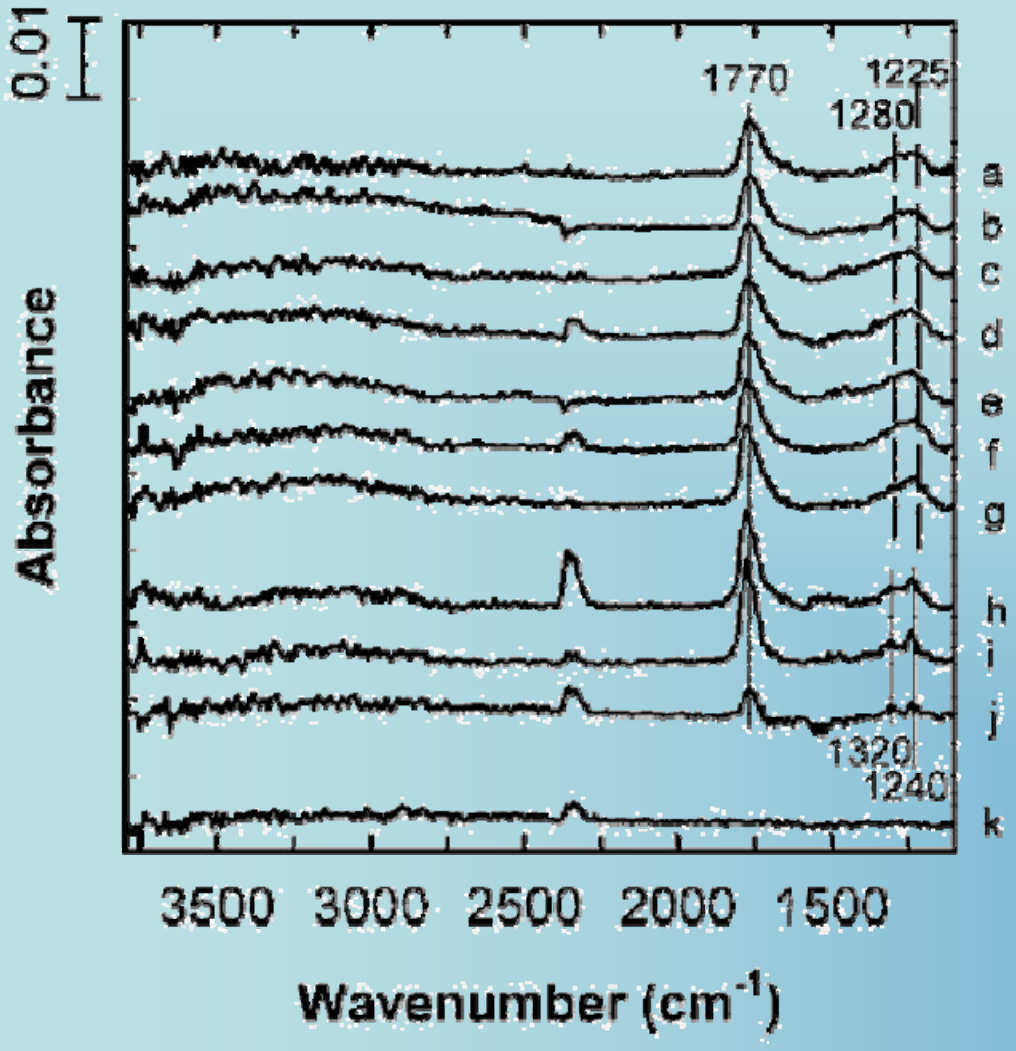
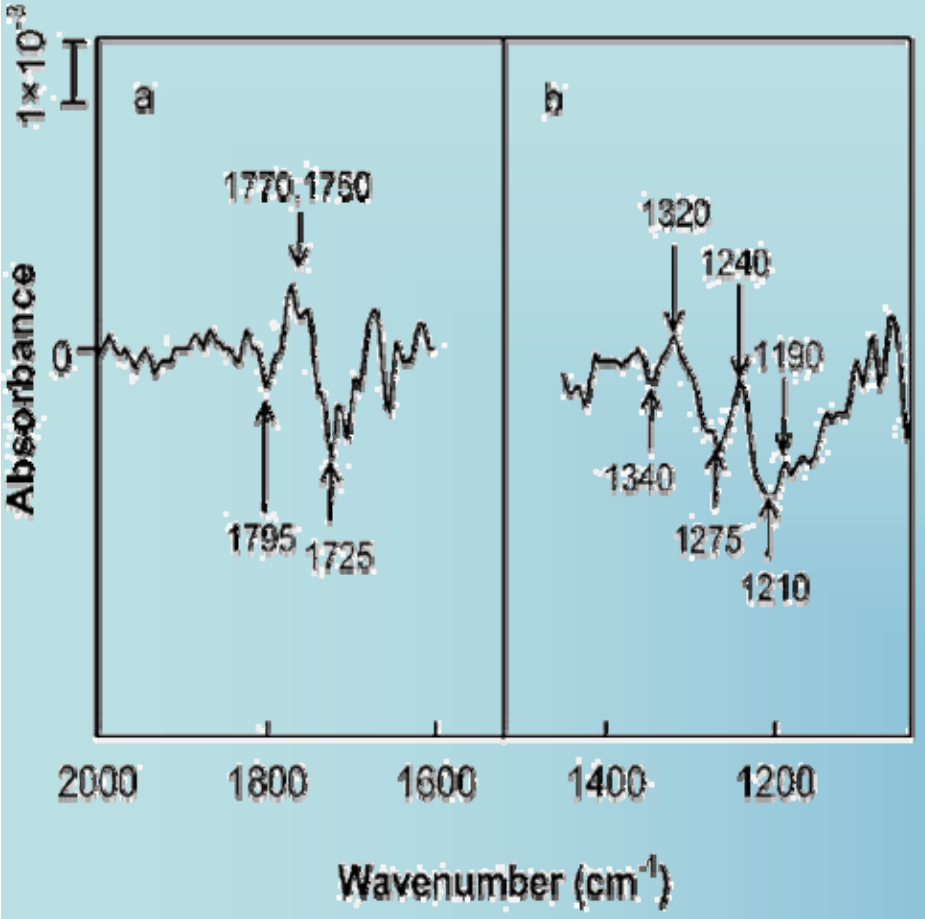


Fig 6 : Adsorption of $C_2H_2O_4$ on the Cu surface as a function of temperature (155 -244 K)

- The absorbance of the 1770 cm^{-1} band increases slightly and the bandwidth narrows
- new bands have appeared at 1320 and 1240 cm^{-1} on increasing the temperature (h-j)
- sI-$C_2H_2O_4$ have lower binding energy than sII-$C_2H_2O_4$
- When the$C_2H_2O_4$ layer is heated surfaces are annealed and defects (surface and within the layer) are reduced



Difference spectrum representing subtraction of an IR spectrum of $C_2H_2O_4$ on the Cu surface at 155K from the corresponding IR spectrum at 225 K

(a) for $\nu_{C=O}$ bands and (b) for ν_{C-O} and δ_{COH} bands

- The peaks at 1795, 1725, 1340, 1275, and 1210 cm^{-1} are associated with the desorbed species up to 225 K (>T_d of sI-$C_2H_2O_4$)
- The species are either on the top surface layer or at the defect sites and these molecules desorbs first
- The desorbed $C_2H_2O_4$ (sI-$C_2H_2O_4$) is associated with weakly bonded $C_2H_2O_4$ molecules
- The peak at 1795 cm^{-1} is due to surface $\nu_{C=O}$ mode
- The peaks at 1770, 1750, 1320, 1240, and 1190 cm^{-1} correspond to the species existing on the Cu surface at 225 K
- The existing the $C_2H_2O_4$ (sII-$C_2H_2O_4$) is associated with strongly H-bonded $C_2H_2O_4$ analogous to solid $C_2H_2O_4$

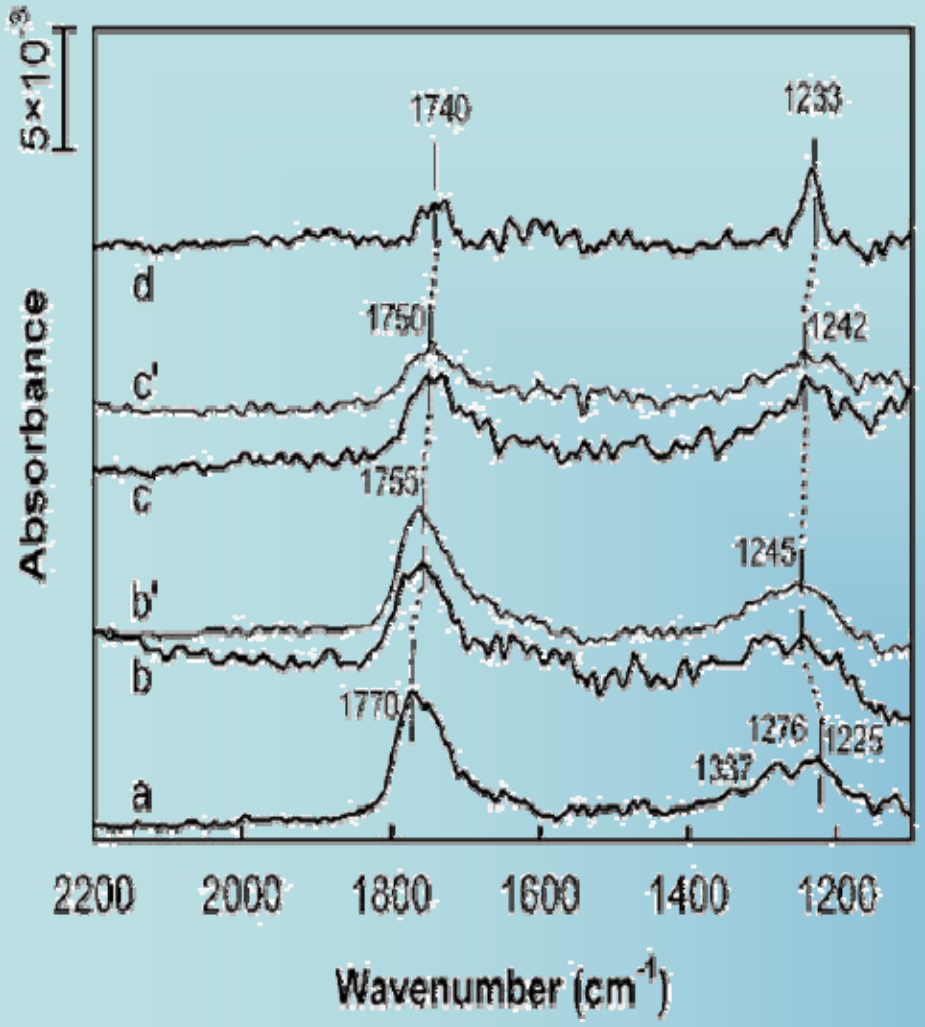


Fig 8: Difference spectra for $C_2H_2O_4$ and ice on the Cu surface at 155 K

(a) 6.2 L $C_2H_2O_4$/Cu surface

Subtraction of a 200 nm H_2O/Cu from 205 nm H_2O/5.8 L $C_2H_2O_4$/Cu

(b') RAIR spectrum for 4 nm H_2O/6.3 L $C_2H_2O_4$ /Cu surface this spectrum reveals the spectral features at the interface of H_2O and $C_2H_2O_4$

(C) Subtraction of C2H2O4/H2O/Cu from 215 nm H_2O/Cu

(c') Subtraction of $C_2H_2O_4$/H_2O/Cu from 500 nm H_2O/Cu

(d) Difference spectrum of$C_2H_2O_4$+H_2Ocodeposited on the Cu surface

Adsorption of $C_2H_2O_4$ and H_2O on Cu Surface

- It can be seen that the $\nu_{C=O}$ band at 1770 cm^{-1} is shifted to a slightly lower frequency ~1755 cm^{-1}(15 cm^{-1} red-shift)
- The ν_{C-O} band at 1225 cm^{-1} shifts to a higher frequency, ~1245 cm^{-1}(20 cm^{-1} blue-shift)
- This might be due to the increasing H-bonding interactions between COOH and ice
- The interaction results in a longer C=O bond length (weaker carbonyl bond C=O) and a shorter C-O bond length (stronger C-O bond)
- The Adsorbed $C_2H_2O_4$ has two states (sI- and sII-$C_2H_2O_4$) on the Cu surface
- It is unknown which of the two states is favored to interact with the ice film

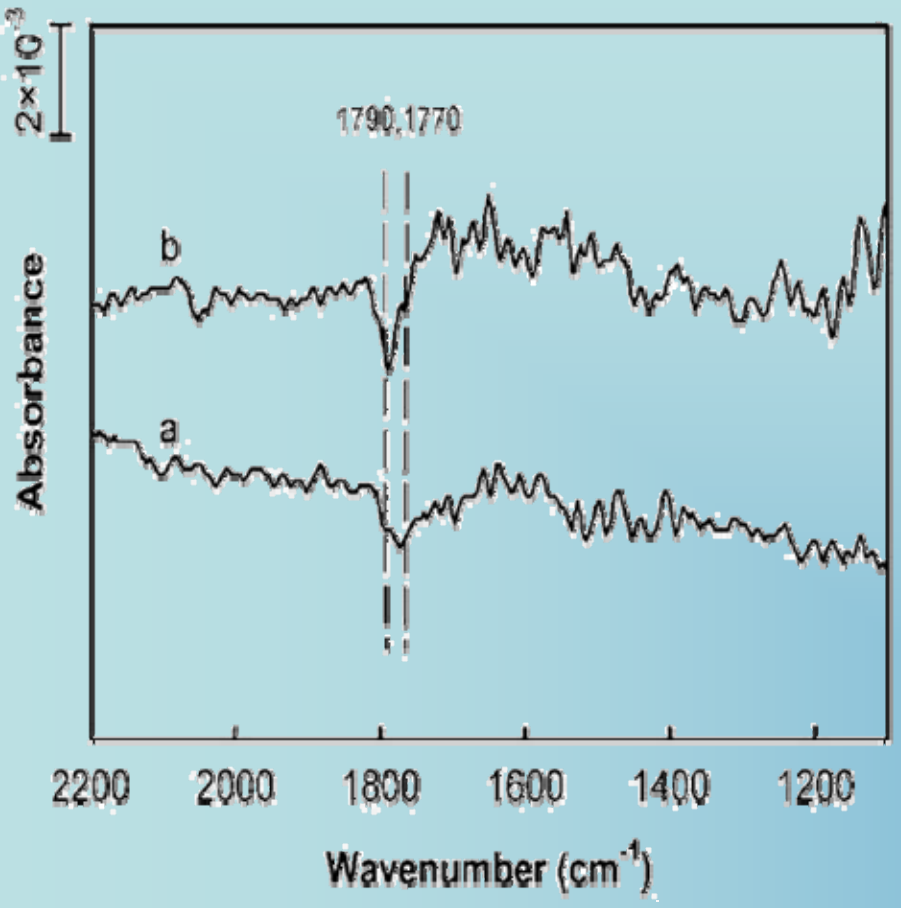


Fig 9 (a) Subtraction of the RAIR spectrum (a) in Figure 8 to spectrum (b) in Figure 8

(b) Subtraction of a 6.5 L $C_2H_2O_4$/Cu spectrum from a difference spectrum for 50 nm H_2O/6.5 L $C_2H_2O_4$/Cu spectrum

- Spectrum (a) reflects the surface and interface vibrational modes of $C_2H_2O_4$
- The peak at 1790 cm^{-1} can be assigned to the $\nu_{C=O}$ mode of $C_2H_2O_4$ on the surface or at the interface
- The band at 1770 cm^{-1} could represent the $\nu_{C=O}$ vibration either at the interface or in the $C_2H_2O_4$ layer (many $C_2H_2O_4$ spectra have this frequency)
- The peak at 1790 cm^{-1} can be assigned to the $\nu_{C=O}$ mode of $C_2H_2O_4$ on the surface or at the interface
- The ice-film thickness does not change the frequencies of the bands and the presence of interfacial $\nu_{C=O}$ mode is independent of thickness

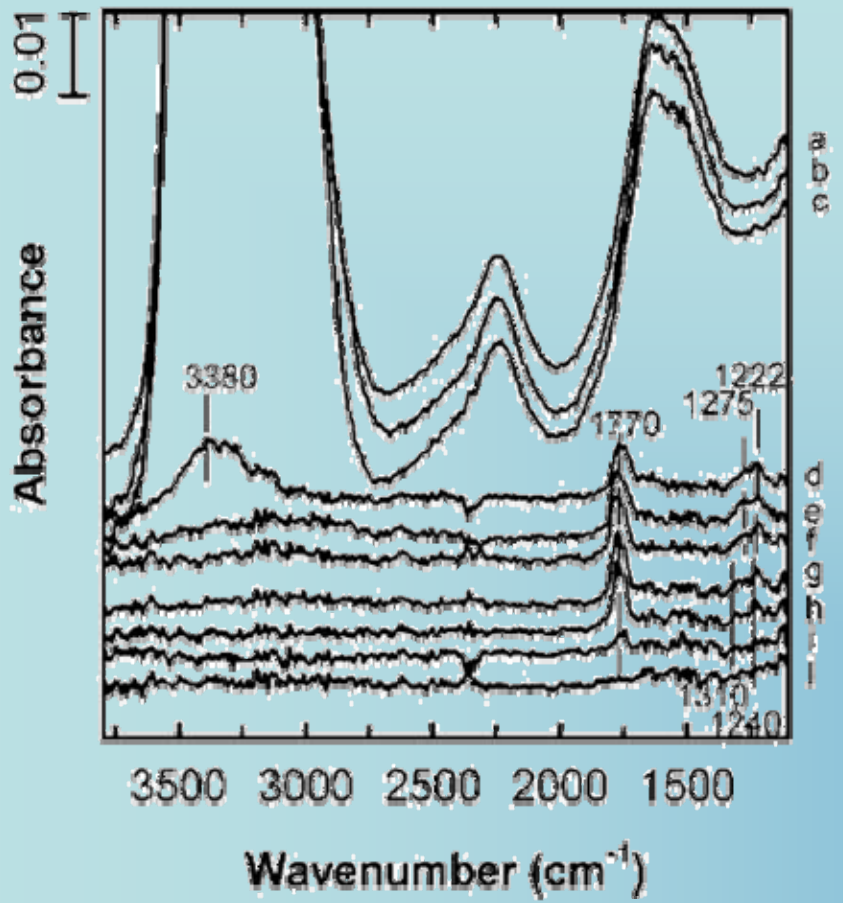


Figure 10. RAIR spectra for 680 nm ice deposited on a 6.8 L $C_2H_2O_4$ covered Cu surface as a function of temperature

For spectra a-k, the corresponding temperatures are 155, 161, 172, 183, 194, 205, 217, 225, 237, and 283 K

- Spectra(e-i) is nearly the same as those in spectra (f-j) in Figure 6
- As the temperature increases frequency shifts from 1222 to1240 cm^{-1} and the bandwidth decreases
- This suggests that the ice adlayer does not dramatically alter the structure of the $C_2H_2O_4$ layer
- Nevertheless, the $C_2H_2O_4$ layer undergoes some structural modification, from less well ordered structure to more highly ordered structure, at the T_d of sI-$C_2H_2O_4$
- Desorption of ice on the $C_2H_2O_4$ layer has minimal impact on the structure of the $C_2H_2O_4$ layer

Adsorption and desorption of $C_2H_2O_4$ on Ice-Covered Cu Surfaces at 155 K ($C_2H_2O_4/H_2O/Cu$)

- IR spectral features for $C_2H_2O_4/H_2O/Cu$ are similar to those for $H_2O/C_2H_2O4/Cu$ at 155 K and they are not affected by the ice thickness
- The $C_2H_2O_4$ layer and the ice film are little mixed at 155 K as T_d of H_2O < T_d of $C_2H_2O_4$
- The change of ice T_d indicates that the $C_2H_2O_4$ adlayer on the H_2O/Cu surface alters the ice desorption behavior
- The changes in desorption profile for both $C_2H_2O_4$ and ice suggest that the structure of the $C_2H_2O_4$-ice film altered during the heating process
- H_2O molecules diffuse through the $C_2H_2O_4$ layer and then desorbs to the gas phase (grain boundaries and defects)
- The interaction between $C_2H_2O_4$ and ice is weaker than the interaction between $C_2H_2O_4$ and$C_2H_2O_4$ (stronger H-bonds, the sublimation enthalpy for $C_2H_2O_4$ is 98.0 kJ mol^{-1})

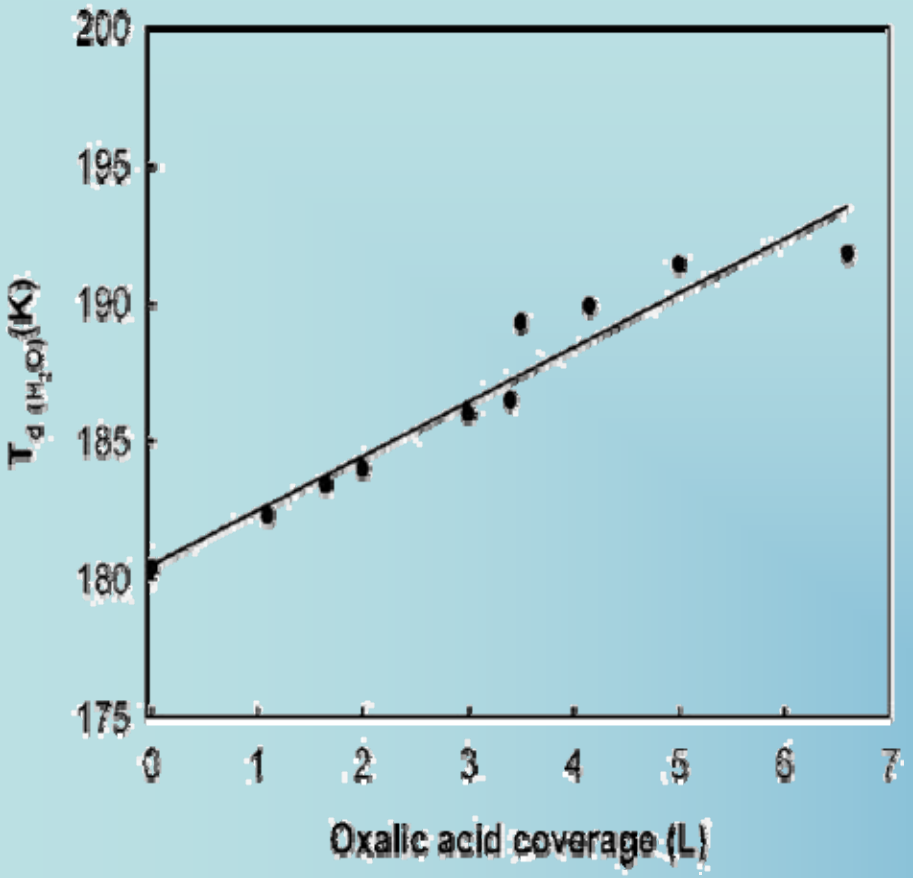


Figure 11. Desorption temperature T_d of ice as a function of $C_2H_2O_4$ coverage, in the $C_2H_2O_4/H_2O/Cu$ system

- The plot indicates that the ice desorption temperature is linearly proportional to $C_2H_2O_4$ coverage
- The ice T_d is limited by H_2O diffusion through the $C_2H_2O_4$ layer
- H_2O takes longer time to diffuse through a thicker $C_2H_2O_4$ layer
- The diffusion time can be estimated using $t \approx d/2D$, where d is the thickness of the $C_2H_2O_4$ layer and D is the diffusion coefficient of H_2O in $C_2H_2O_4$
- The temperature is linearly proportion to the time and thus the ice T_d is linearly proportional to $C_2H_2O_4$ coverage
- Desorption of ice in the $C_2H_2O_4/H_2O/Cu$ system is governed by the diffusion of H_2O through the $C_2H_2O_4$ layer

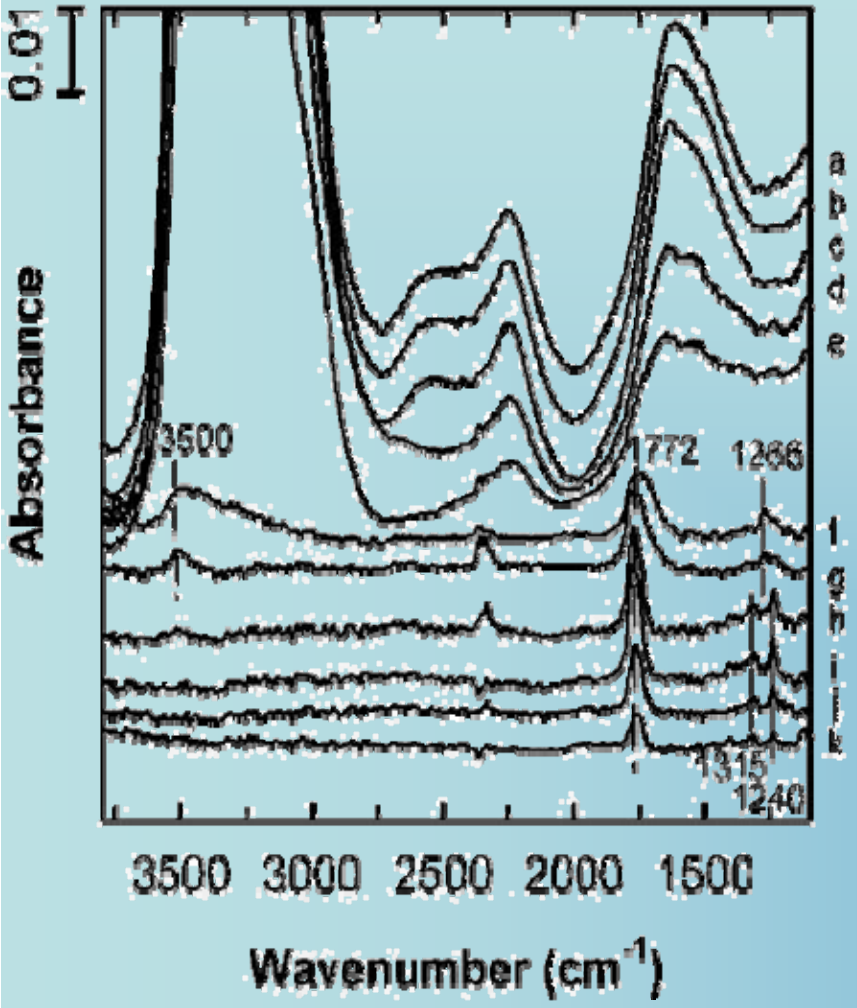


Figure 12. RAIR spectra of 6.9 L $C_2H_2O_4$ layer deposited on the 680 nm ice-covered Cu surface as a function of temperature

- Bands at 3500, 1266 and a broad band at 1772 cm^{-1} suggests that H_2O forms a complex $\{C_2H_2O_4 \cdot (H_2O)_n\}$ with $C_2H_2O_4$ during the TPD process
- Both the 3500 and the 1266 cm^{-1} bands disappeared (while the broad 1772 cm^{-1} band becomes narrower) before temperature reached the T_d of sI-$C_2H_2O_4$ (215 K)
- This suggests that the complex is metastable and exists at temperatures below the T_d of sI-$C_2H_2O_4$
- Formation of complex $C_2H_2O_4 \cdot (H_2O)_n$ depends not only on the stoichiometric ratio of H_2O and $C_2H_2O_4$ but also on the specific orientations of theH_2Omolecules that encounter$C_2H_2O_4$
- $C_2H_2O_4$ undergoes structural modifications at the T_d of sI-$C_2H_2O_4$, after H_2O is desorbed from the film

Co-adsorption and desorption of $C_2H_2O_4$ and H_2O on the Cu Surface at 155 K

$C_2H_2O_4$+H_2O/Cu

- $C_2H_2O_4$ is anticipated to be homogeneously mixed
- Comparing Spectrum (d) in Figure 8 with an IR spectrum of gas-phase $C_2H_2O_4$ shows that the $\nu_{C=O}$ band is red-shifted from 1820 cm^{-1} in the gas phase to ~1740 cm^{-1} in the $C_2H_2O_4$-ice mixture
- The magnitude of the red-shift is reasonable, because $\nu_{C=O}$ is 1688 cm^{-1} for oxalic acid dihydrate
- The H_2O desorption temperature increases in the following order
- $C_2H_2O_4/H_2O/Cu > C_2H_2O_4+H_2O/Cu > H_2O/C_2H_2O_4/Cu \approx H_2O/Cu$ for comparable ice-film thicknesses and oxalic acid coverages

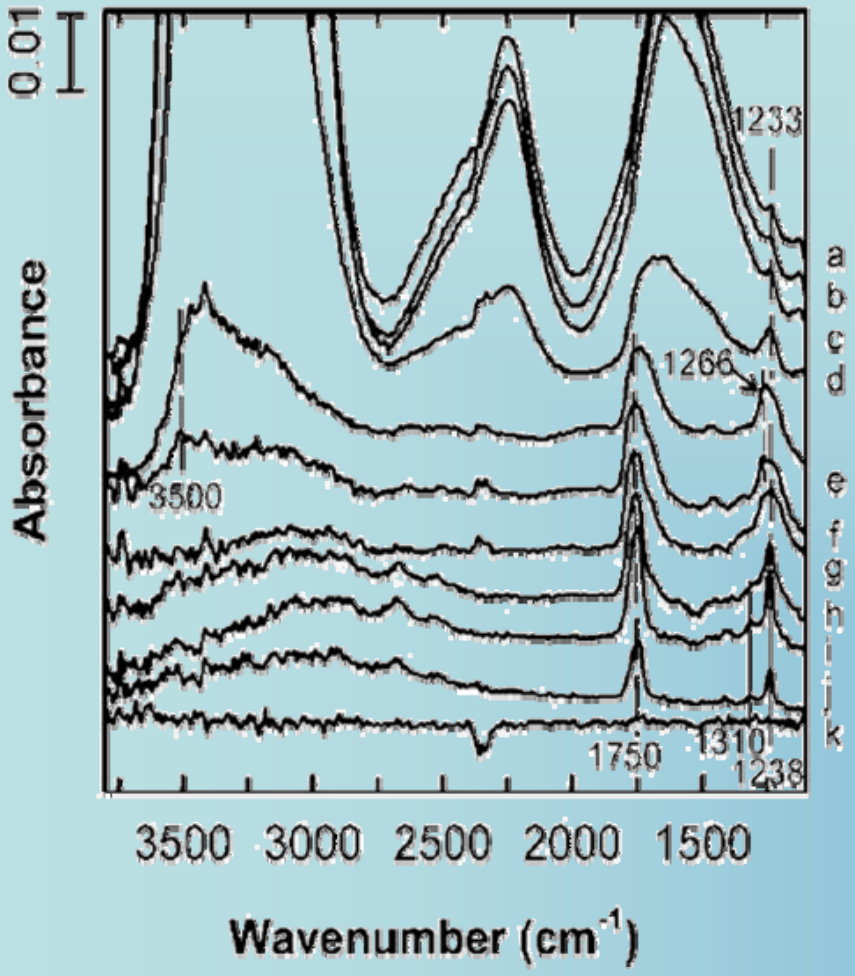


Figure 13: RAIR spectra of codeposited 6.8 L $C_2H_2O_4$ and 710 nm ice on the Cu surface .For a-k, the corresponding temperatures are 155, 161, 172, 183, 189, 194, 205, 217, 225, 237, and 242 K

- A band at 1233 cm^{-1} was observed in spectra(a-d) at T ≤ 183 K
- At 189 and 194 K bands at ~3500,1750, and 1266 cm^{-1} were observed
- The band at 1750 cm^{-1} is broad and appears to have overlap with lower-wave number bands (1690cm^{-1})
- A metastable $C_2H_2O_4 \cdot (H_2O)n$ complex is formed However the metastable complex disappears at 205K as indicated by the loss of the bands at 3500,1750 and 1266 cm^{-1}
- The complex exists in a narrow temperature region
- After the complex is broken down, $C_2H_2O_4$ is likely to form an ultra thin film over the Cu surface
- The $C_2H_2O_4$ layer undergoes a structural modification at ~217 K (bands at 1750, 1310, and 1238 cm^{-1})
- $C_2H_2O_4$ molecules are surrounded by H_2O molecules via the van der Waals and H bonding interactions in the codeposited mixture at 155 K

Conclusion

- The analysis of RAIRS and TPD data suggests that interaction between the ice film and $C_2H_2O_4$ layer occurs primarily at the interface
- Neither hydrogen oxalate nor oxalate is formed suggesting that no H_2O-induced deprotonation of $C_2H_2O_4$ takes place in three systems namely H2O/C2H2O4/Cu, $C_2H_2O_4/H_2O$/Cu, and$C_2H_2O_4$+H_2O/ Cu over the temperature range 155-283 K
- The H_2O T_d for CH_3COOH/H_2O is ~7 K higher than that for H_2O/ CH_3COOH
- The interaction between H_2O and H_2O, via H-bonds, is weaker than that between $C_2H_2O_4$ and H_2O
- Ice-$C_2H_2O_4$ interaction is not sufficiently strong to deprotonate $C_2H_2O_4$ on/in ice hence ice cannot ionize $C_2H_2O_4$ into HC_2O_4 or C_2O_4 2^- at 155 K or above
- A metastable oxalic acid-ice complex, $C_2H_2O4 \cdot (H_2O)_n$, was observed during the TPD process in the $C_2H_2O_4/H_2O$/Cu and H_2O+$C_2H_2O_4$/Cu systems
- $C_2H_2O_4$ is not in a dissociative state in ice/snow in the polar boundary layer (~240 K) or at upper tropospheric temperatures