Adsorption of Organic Isomers on Water Ice Surfaces: A Study of Acetic Acid and Methyl Formate

M Bertin, C. Romanzin, X.Michaut, P.Jeseck and J.H Fillion.
UPMC Univ Paris 6, LPMAA, UMR 7092,F-75252 Paris, France

J. Phys Chem. C **2011**,*115*,12920

Rabin Rajan J Methikkalam

1/10/2011

Introduction

- Interaction between small organic molecules and water ice attracted much attention due to its relevance in several fields of interests.
- From fundamental molecular physics to the chemistry of the polar stratosphere and the interstellar medium (ISM).
- Because of their presence as volatile organic compounds (VOCs) in region of the upper troposphere to lower stratosphere where water ice particles are also present.
- Oxygen bearing molecules like acetic acid, methyl formate interaction with ice are important as they are present and are detected in various astro physical studies.

- Thermal desorption studies of ice mixtures of organic molecules and water, mimicking ISM ice compositions and phases have been intensively studied.
- Here the experimental study focuses on the surface adsorption of two organic isomers, Acetic Acid (CH_3COOH) and Methyl Formate ($HCOOCH_3$) deposited on water ice films on a temperature range 80-200K.
- The two isomers have comparable dipole moment, but the difference in desorption behavior is associated with specific inter and intra molecular interactions like H-bonding and functional groups.
- The experiment have been carried out using TPD and RAIRS simultaneously.
- Both multilayer and sub-monolayer interactions are studied.

Experimental Section

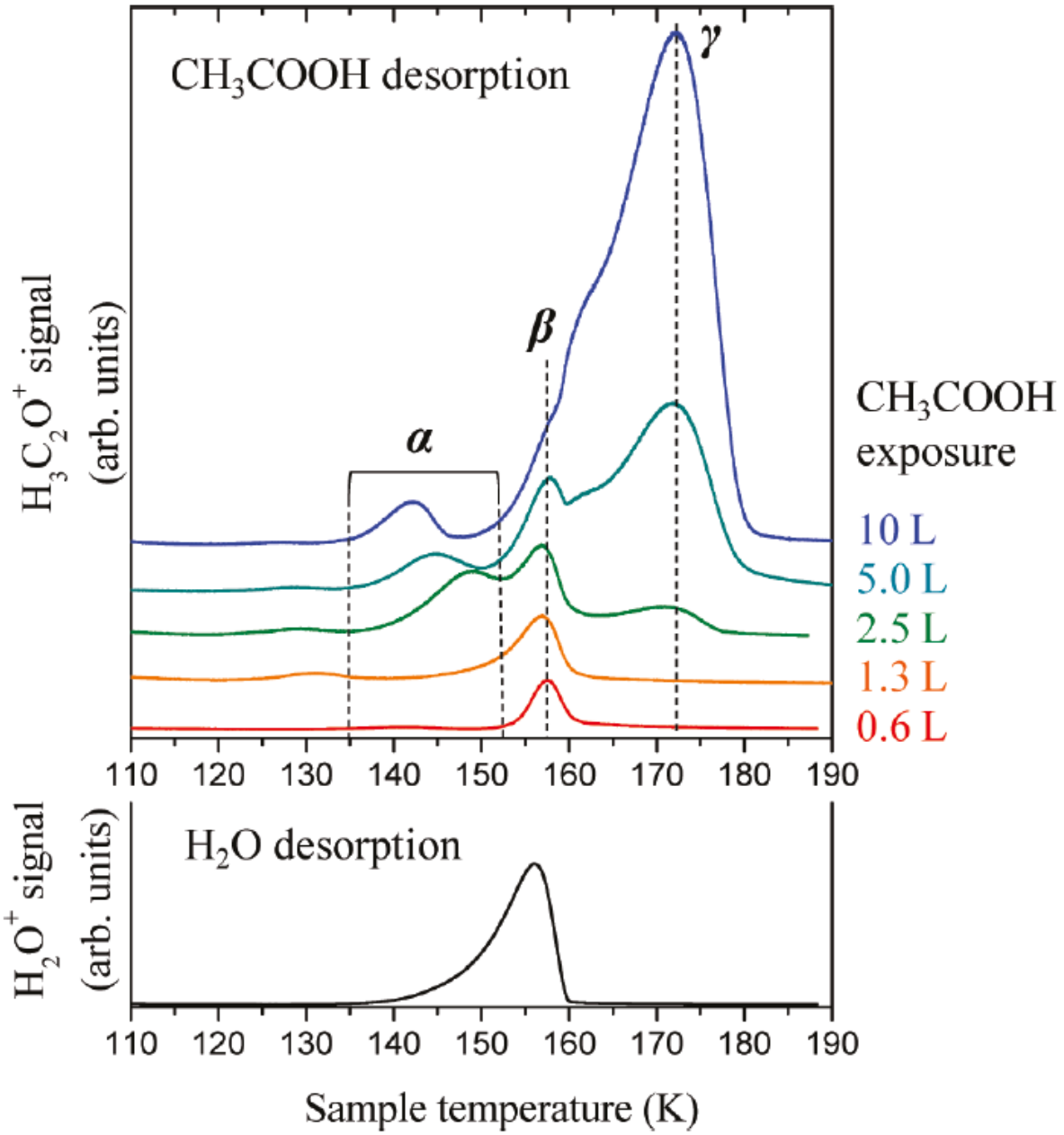
- A He-compression closed cycle cryostat is housed in an Ultra High Vacuum chamber (base pressure~ 10^{-10} Torr).
- A polycrystalline Gold substrate is fixed at the cold end and its temperature can be varied from 10 to 350K.
- The heating regulation allows the control of the temperature between 0.1 and 10K min^{-1}.
- Amorphous water ice and crystalline water ice surfaces are deposited on the gold substrate by adjusting the temperature and pressure and their structure confirmed by IR measurement of OH dangling bond and the desorption signal of the amorphous phase in TPD curves.
- Acetic Acid and Methyl Formate are deposited on top of ice covered gold substrate at 80K

Results and discussion

1.1 Acetic acid

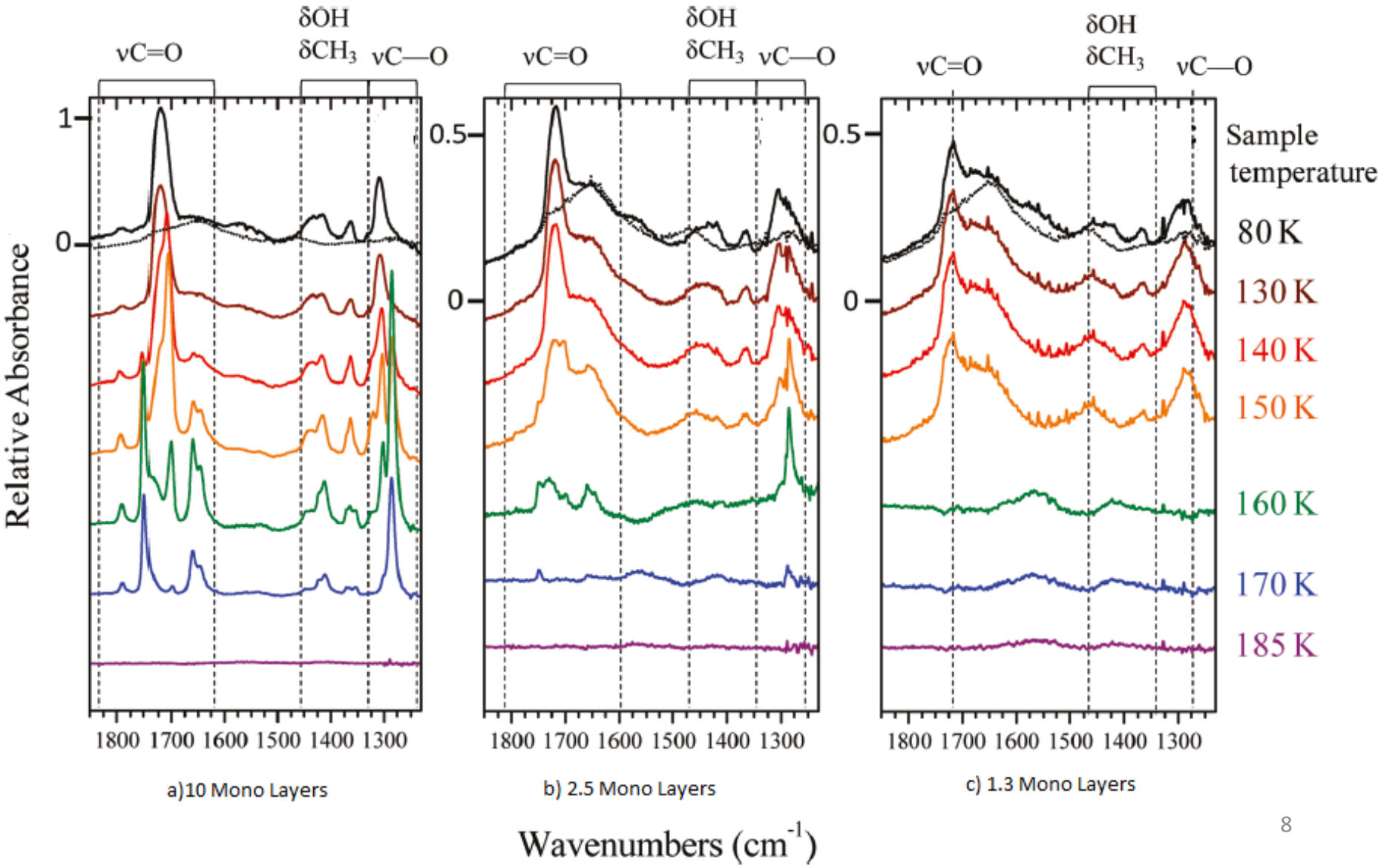
- Acetic Acid on water is studied by many researchers, but mostly with heavy number of monolayers.
- Here they are studying about a few monolayers to get more on a single molecule which is more relevant astrophysically/stratospherically.
- TPD and RAIR spectra are presented.
- Acetic acid first layer forms a strong bond with water.
- Multilayer remain in cyclic dimer. Increasing temperature a phase change from cyclic dimer to chain like polymer occurs, and the underlying water molecules desorb through it while acetic acid remains in the condensed phase.

1.1.1 TPD Spectra of Acetic acid



α (135K-145K)	**Multilayer**	**Due to Acetic Acid monomer desorption during dimer to polymer phase change.**
β (150K-160K)	Monolayer	Acetic acid First monolayer desorption with H_2O
γ (upto180K)	Multilayer	Desorption of Acetic Acid chain like H-bonded polymer.

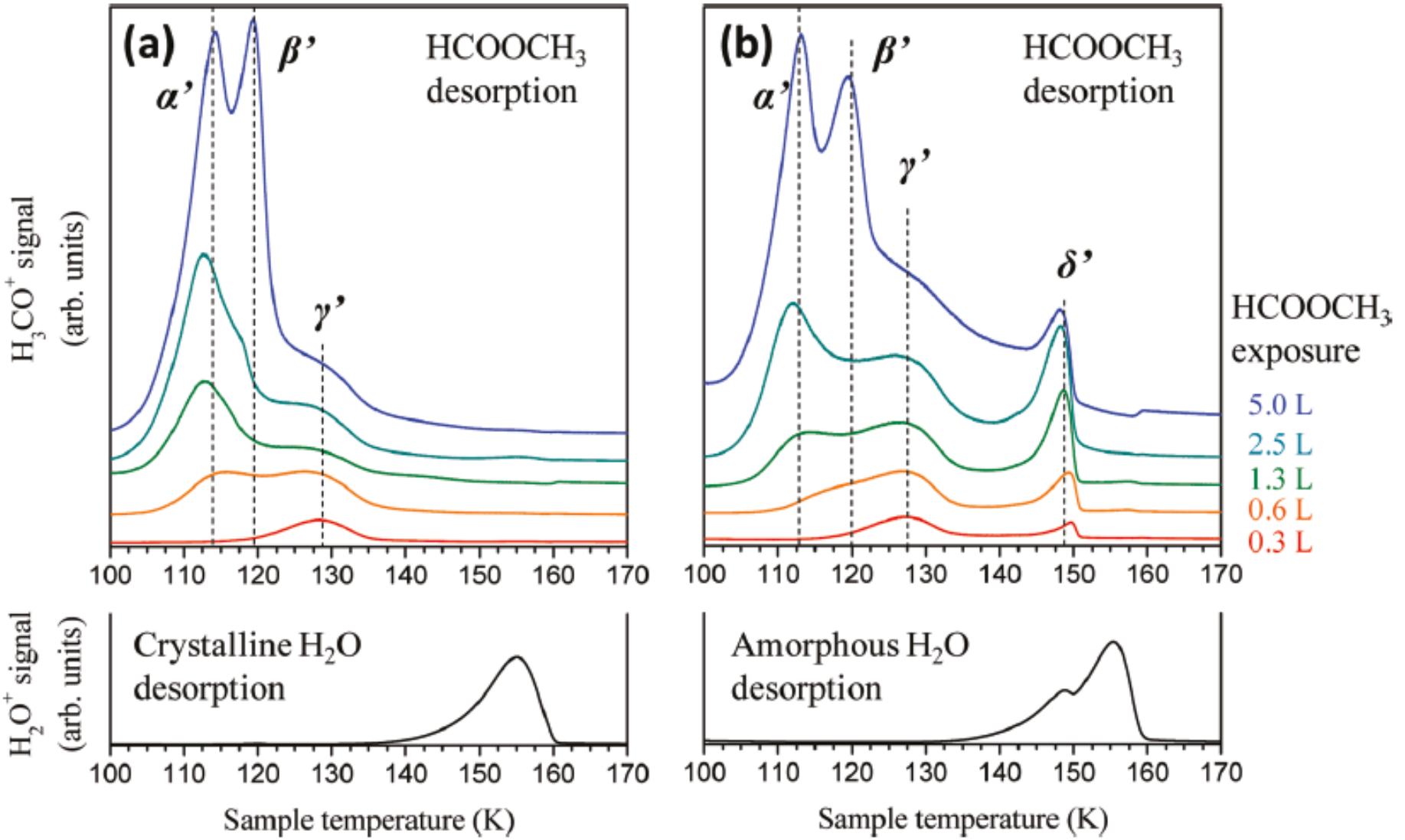
1.1.2 RAIR Spectra of Acetic acid



1.2 Methyl Formate

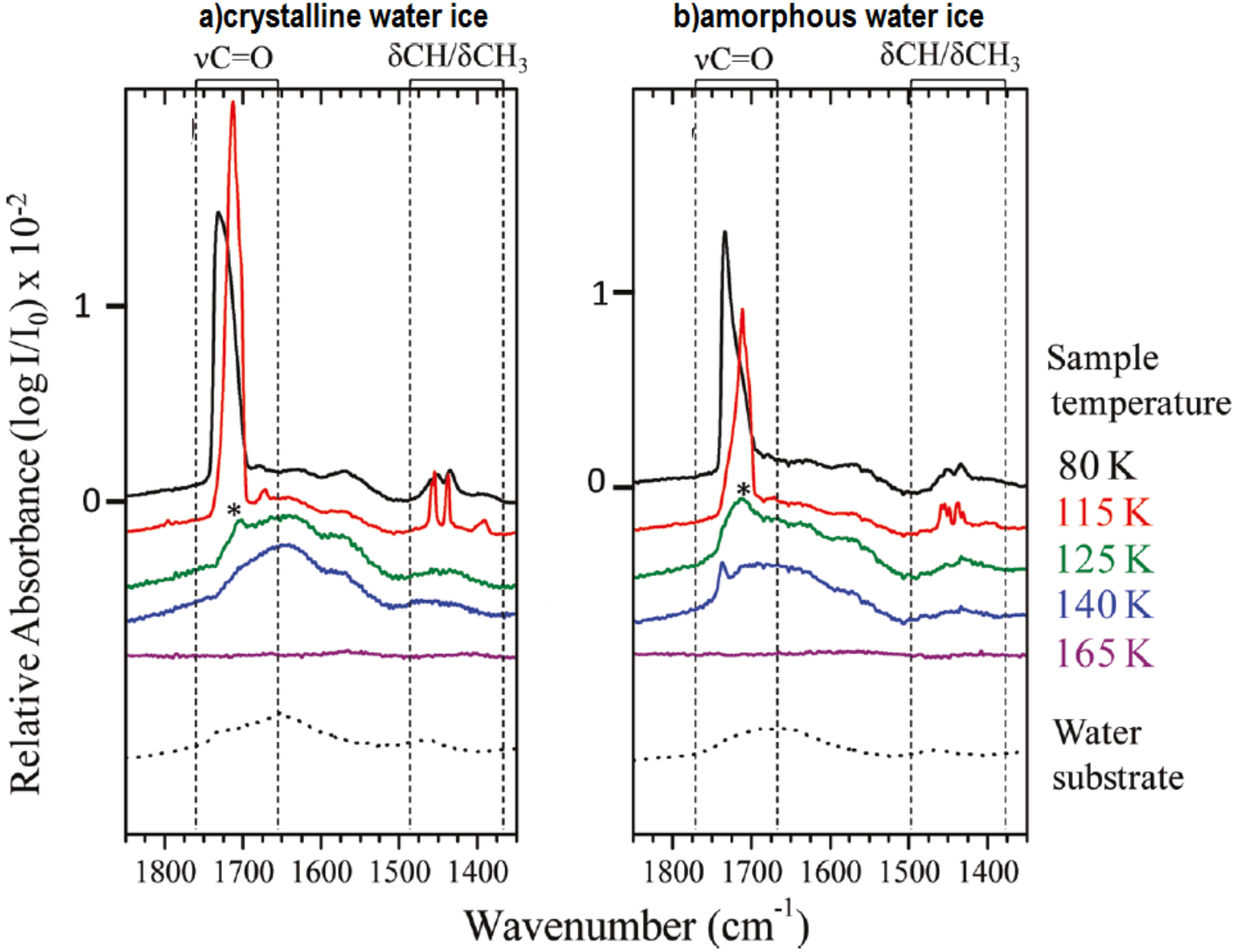
- Methyl Formate adsorption on H_2O unlike Acetic Acid is not much studied.
- In the present work same experiment protocol for the study of Acetic Acid is also followed for Methyl Formate.
- TPD and RAIR Spectra are presented.

1.2.1 TPD Spectra of Methyl Formate



α’(112K)	Multilayer	Amorphous to crystalline phase change of Methyl Formate
β’(120K)	Multilayer	Amorphous to crystalline phase change of Methyl Formate
γ’(130K).	Monolayer	Methyl Formate interaction with water(Monolayer Desorption)
δ’ (152K- only for Amorphous ice surface)	Volcano effect	Due to the trapped Methyl Formate molecules in Amorphous ice surface during phase change.

1.1.2 RAIR Spectra of Methyl Formate



- The energy adsorption of first layer for Methyl Formate is calculated using Polanyi-Wigner equation which is given as
  $E_{ads}(n) = -KT \ln(\psi d / \mathit{Vn})$.

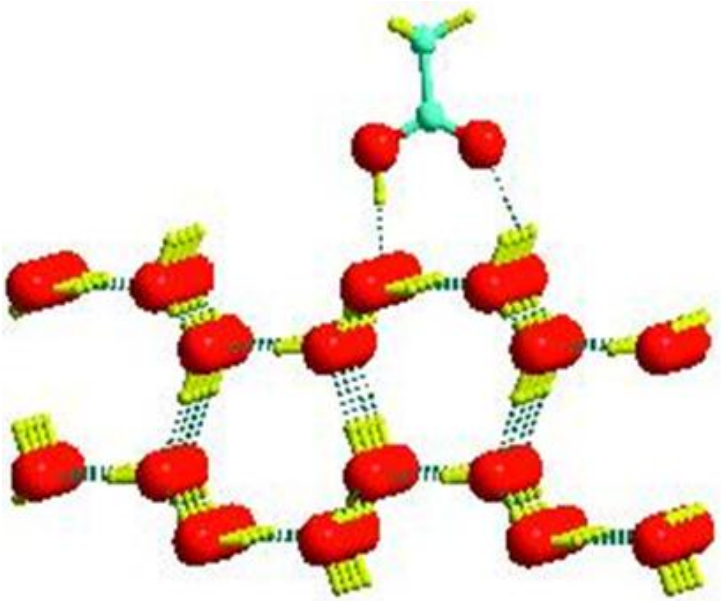
- The E_{ads} for Methyl Formate on amorphous ice surfaces is found to be 37± 4 and that for crystalline ice surface was found to be 38± 4.

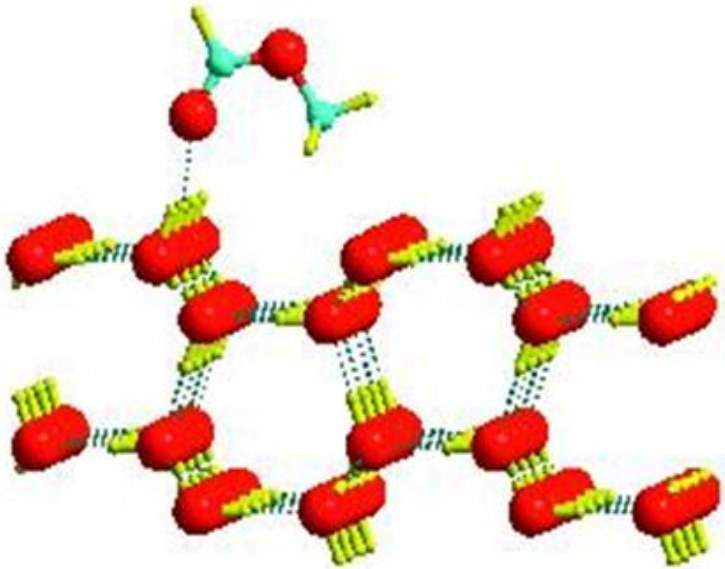
Summary and Conclusions

- Temperature-induced desorption of condensed Acetic Acid and Methyl Formate from water ice surfaces has been studied by means of TPD and RAIRS technique.
- Each desorption feature observed in TPD has been attributed to a given molecular organization of Acetic Acid and Methyl Formate molecular overlayer, differentiating multi layer and submonolayer.
- The adsorption energies of Acetic Acid and Methyl Formate on water surfaces are very different.
- The difference is mainly due to the different functional groups and their extent of H-bonding.

- Acetic acid is having strong interaction as it can have two H-bonding with H_2O, while Methyl Formate which can have only one H-bonding with H_2O molecule is found to have less interaction.
- Methyl formate interaction with both crystalline and Amorphous water ice surfaces were studied while, Acetic acid interaction with crystalline ice surface was only done.
- This is because submonolayer Acetic Acid molecules are also expected to be released with H_2O molecules together with volcano effect will make it difficult to isolate the peak and to derive its interaction energy with the surface.

- The method presently used for Acetic Acid and Methyl Formate could be extended to other small organics with similar molecular weights, but with other chemical groups such as propanal.
- Further investigations with ices presenting higher porosity and comparison between pure, mixed and layered ices are needed to estimate in detail the role played by this effect in an astrophysical context.
- The different chemical routes of formation of each isomer, presenting different efficiencies, should also be considered as they may significantly influence the gas-phase abundance ratio of organics in the Interstellar medium (ISM).





Thank you all….