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VUV Photolysis of CH₄-H₂O mixture in methane-rich ices: Formation of large complex organic molecules in astronomical environments.

Lahouari Krim^{*}, Mindaugas Jonusas

Sorbonne Université, CNRS, De la Molécule aux Nano-Objets: Réactivité, Interactions, Spectroscopies, MONARIS, 75005, Paris, France.

** Corresponding author: Lahouari.krim@upmc.fr*

Abstract:

The present work aims to highlight the influence of water molecules in the photodecomposition of methane ice and reveal the photoproducts formed in solid phase upon VUV irradiation of CH₄-H₂O mixture in methane-rich ices. The analysis of our IR spectra shows that even with very low concentrations of water in methane ices, several oxygenated hydrocarbons are formed as photoproducts derived from the photodecomposition of water and methane at cryogenic temperatures. We show that both alka[e]nes and oxygen bearing organics are efficiently formed at temperatures as low as 3 K. However, while the IR signatures of the alka[e]nes such as C₂H₆, C₂H₄ and C₂H₂ dominate the IR spectra of the irradiated CH₄-H₂O ices at temperatures lower than 50 K, the heating of the sample to 110 K reveals the formation of large carbon chain complex organic molecules such as ethanol, pronanol, porpanal and glycolaldehyde.

Keywords: astrochemistry, laboratory simulation, IR spectroscopy, complex organic molecules,

Introduction

Saturated and unsaturated hydrocarbons are likely formed in aerosol particles of CH₄-rich atmospheres of planets and moons such as Saturn and Saturn's huge moon Titan. The icy surfaces of some solar objects such as Pluto, Saturn and Titan may host giant dunes of hydrocarbons like methane and ethane ice dunes which have been reported through images¹ from the New Horizons flyby of Pluto in July 2015. Additionally, methane and ethane mixed ice clouds are both present in the troposphere and stratosphere of Titan atmosphere². In this sense, photochemistry of methane ices has been investigated by several groups in pure methane and rare gas matrices in order to explore the formation routes of carbon chains and hydrocarbon detected towards planetary atmospheres and molecular clouds. Wu et al³ studied, using synchrotron vacuum-ultraviolet light, the photolysis of methane dispersed in solid neon. they showed that carbon chains up to five carbon atoms are easily formed at cryogenic temperatures and might be part of the chemical composition of methane rich regions in space. Similar investigations carried out by Lin et al⁴ underlined the formation of large carbon chains up to 20 carbon atoms and other various radical saturated and unsaturated hydrocarbons. The cryogenic synthesis of CH, CH₂, CH₃, C₂H₂, CH₂H₃, C₂H₄, C₂H₅ and C₂H₆ has been examined by Bennett et al⁵ through energetic electrons irradiation of pure methane ices to mimic the role of cosmic-ray particles in the chemical transformation of methane which can be the source of large complex molecules including prebiotic species⁶. Laboratory studies of methane ice photolysis have been extended to molecular ices relevant to cometary and interstellar ices and also to icy satellites of planetary systems in order to identify the complex organic molecules formed in astronomical environments. Several studies have been focused in photolysis and radiolysis of CH₄-H₂O mixed ices to probe the formation of oxygen bearing species already detected or looked for in space such as ethanol (C₂H₅OH), dimethyl ether⁷ (CH₃OCH₃), methyl acetate⁸ (CH₃COOCH₃), ethyl formate⁸ (C₂H₅OCHO) and glycolaldehyde⁹ (HOCH₂CHO). Moore et al^{10,11} highlight radiation experiments in H₂O rich ices containing astrochemical species relevant such as CO, C₂H₂ and CH₄. They identified many complex species which depend strongly on the chemical composition of the irradiated ices. In the case H₂O-CH₄ mixed ices, three H₂O-rich ices with different H₂O:CH₄ concentrations, 2 : 1, 7 : 1, and 15 : 1, have been considered. The IR spectra recorded after irradiation showed the formation of C₂H₆, C₃H₈, CH₃OH, C₂H₅OH, H₂CO, CH₃CHO in addition to CO and CO₂. Although the H₂O:CH₄ concentrations have been specifically chosen based on astronomical detections where CH₄ is highly less abundant than water; Bockelee-

Morvan et al¹² reported from Rosetta observations that in the coma of comet 67P, methane abundance relative to water is ranged between 0.2 and 0.5 % ; these laboratory simulations carried out in order to provide significant data correlating to such observations, cannot reveal the nature of all chemical species formed during the photo processing of CH₄-H₂O mixed ices in water rich environment configuration. In fact even in the case of experiments performed with the lowest concentration of water (H₂O:CH₄ = 2 : 1), the IR spectra recorded by Moore and Hudson are dominated by the huge wide absorption bands of water ice which hide many reaction products formed during the photolysis processing. In order to study the influence of H₂O molecules in the photo-induced decomposition of CH₄ in solid phase, we have investigated the photolysis of CH₄-H₂O mixed ices in CH₄-rich environments. Counter to H₂O-ice which has strong absorption signals in practically all the MID-IR spectral region; the H₂O-twisting mode IR signal is expanded in the 500-1000 cm⁻¹ spectral region, H₂O-bending mode absorb in a wide spectral range 1400-1700 cm⁻¹ and the 2800-3700 cm⁻¹ spectral region is congested by the huge absorptions of OH vibrations; the IR absorption signals of CH₄-ice, even with very high concentration of methane, consist of two main relative narrow bands at 1301 and 3012 cm⁻¹. Consequently, the isolation of H₂O + CH₄ photo-induced solid state reaction in methane-rich environment will allow a better identification of the reaction products derived from the simultaneous solid state decomposition of H₂O and CH₄.

Experimental section

The experimental setup used in the present study has already been described in previous articles¹³, thus only important features are mentioned hereafter. The experiments are performed under ultra high vacuum at 10⁻¹⁰ mbar. A Rh-plated copper mirror is used as a substrate to condense the reactants and to form the CH₄-H₂O mixed ices. CH₄ (99.999%) purchased from Messer and demineralized and degassed H₂O are co-condensed pure at 3 K. The photolysis of our samples during 30 min, have been performed using a VUV lamp with a flux around 10¹⁵ photons.cm⁻².s⁻¹ (Hamamatsu L10706 UV) and photon outputs of 25% at 121 nm (~10.3 eV) and 75% at 160 nm (~7.7 eV). The infrared spectra of the solid samples before and after photolysis are recorded using a Bruker Vertex 80v Fourier infrared (FTIR) spectrometer in transmission–reflection mode. The sample thickness and the exact amount of CH₄ and H₂O forming the ice have been evaluated, as it will be discussed in the result section, from the IR spectra of CH₄-rich ices by calculating the column densities (molecule cm⁻²) of CH₄ and H₂O. Additionally, IR spectra of pure, methanol, ethanol, propanol and propanal ices

have been recorded under the same experimental conditions and taken as reference spectra to characterize the reaction products which may derive from the irradiation of CH₄-rich ices containing water. In order to reduce the recombination between the photoproducts derived from CH₄ and H₂O dissociations and avoid the formation of hydrated complexes trapped in CH₄-matrix, all the photolysis experiments have been carried out at the lowest temperature reached with our experimental setup that is 3 K. However, the goal of the present work is not to assign all the IR signals of the species formed after photolysis and trapped in CH₄-matrix at 3 K but to have an IR spectrum of heavy oxygenated species which would form through the photo-induced solid state reaction involving H₂O and CH₄. In fact, in addition to promote radical-radical reactions similar to those occurring at the surface of astronomical icy grains, the heating of the irradiated CH₄-H₂O ices from 3 to 110 K allows to remove all alka[e]nes and to reveal the IR signatures of large carbon chain complex organic molecules without being hindered by the absorption bands of water ice. Such IR signatures are very important to be compared to references spectra of astronomically relevant large hydrocarbons.

Results and Discussion

As the present study is devoted to emphasize the influence of water molecules in the photo-decomposition of the solid methane, one should pay attention on the main photoproducts realized from the irradiation of methane ice which has been largely investigated previously^{4,5,14}. As mentioned in the introduction part, many laboratory simulations of energetic decomposition of pure methane ice have been explored in order to underline the role of CH₄ fragmentation in the formation of complex organic molecules on the surfaces of icy bodies in the interstellar medium, comets and solar system objects. In this context, using infrared absorption signatures to indentify the photoproducts, Lin et al⁴ showed that pure methane ices and methane dispersed in solid neon at 3 K subjected to irradiation at wavelengths less than 165 nm lead to the formation of CH₃, C₂H₂, C₂H₃, C₂H₄, C₂H₆, C₄H₂, C₄H₄, C₅H₂, C₈H₂ and C_nH with n = 1–5. They also showed that the adding of small amount of H₂ into solid neon enhanced the formation of long carbon chains C_n species, with n = 3–20. Bennett et al⁵ showed that pure methane ices irradiated at 10 K with energetic electrons lead mainly to the formation of CH, CH₂, CH₃ and C₂H₂, CH₂H₃, C₂H₄, C₂H₅ and C₂H₆. Vasconcelos et al¹⁴ have confirmed, using ions bombardment of methane ice at 16 K, the formation of C₂H₂, C₂H₄, C₂H₆, C₃H₈, C₄H₈ and CH₃. However, they showed that CH₄ ices exposed to energetic radiations lead to the formation of propane C₃H₈ as the most abundant

photoproduct contradicting previous laboratory results which showed that was ethane C₂H₆. They gave a yield ratio [C₃H₈]/[C₂H₆] of the order of 20. In order to reveal the new photoproducts formed upon UV irradiation in methane ices containing small amounts of water, methane-rich samples have been prepared by keeping the concentration of methane constant and varying that of water. Figure 1 shows the IR spectra of three CH₄-rich ices containing small amounts of water with concentrations of CH₄:H₂O = 3 : 1, 6 : 1 and 200 : 1. The assignments of all vibrational modes¹⁵ of CH₄-H₂O ice are directly reported in the figure. The amounts of CH₄:H₂O concentrations have been evaluated from the IR spectra of CH₄-rich ices formed at 3 K. Even though the band strengths of molecular species depend strongly on the environment where they are trapped, we have performed these column densities calculation in order to estimate the relative concentrations ratios [CH₄]/[H₂O]. The column densities n (molecule cm⁻²) of the CH₄ and H₂O can be deduced from the integrated IR intensities of the corresponding characteristic absorption bands¹⁶. In the case of water, the bending mode of H₂O at 1600 cm⁻¹ has been used with the band strength of 1.2 10⁻¹⁷ cm molecules⁻¹ taken from Gerakines et al investigations¹⁷ (the same value has been also predicted by DFT calculations for water monomer¹⁸). For the methane ice, as the samples are CH₄-rich ices, the CH₄ fundamental bands at 1306 and 3015 cm⁻¹ are saturated, we have thus used the combination absorption band of CH₄ at 4202 cm⁻¹ with the band strength¹⁹ of 1.6 10⁻¹⁸ cm molecules⁻¹ to estimate the amount of CH₄ in each sample. Knowing that CH₄ ice at cryogenic temperatures has a density²⁰ of 0.47 g cm⁻³, we have deduced the thickness of our samples around 1 μm. In such samples of methane ices containing small amounts of water, CH₄ molecules form a crystal where H₂O are entrapped. Through this methane matrix isolation, we can distinguish the formation of many water clusters such as (H₂O)_{*n*} where *n* = 1-6 as shown in figure 1. All these complexes absorb in the same spectral region for the bending mode at 1600 cm⁻¹, but they have their characteristic spectral positions in the OH stretching region, ranging from 3800 to 3100 cm⁻¹. The formation of water clusters in CH₄ matrix is in good agreement with the studies carried out by Yamakawa et al²¹. However, we notice that in diluted sample with CH₄:H₂O concentration equal to 200 : 1, only water monomer has been detected (figure 1a). By increasing the amount of water in methane ice (figures 1b en 1c), we favor the formation of water aggregates. The samples containing water clusters (figures 1b en 1c) can also be characterized by monitoring the water aggregate libration through the huge and wide absorption band in the 900 – 600 cm⁻¹ spectral region. Figure 2 shows the global results of the photolysis of CH₄-rich ices containing different amounts of water. Many new signals appear in different spectral regions. The new signals are

due to the photo fragments released from the photo-destruction of CH₄ and H₂O molecules as well as to reaction products formed through recombination between all the photo fragments. In addition to the formation of CO and CO₂ shown in figures 2b, 2d, 2f and which result from the oxidation of methane, other oxygen bearing organics such as alcohols and aldehydes are formed as photoproducts. However, many of the new signals observed in the IR spectra of the irradiated samples, shown in figures 2b, 2d, 2f, have already been observed previously and assigned to alka[e]nes which are proper photoproducts realized from methane such as C₂H₆, C₂H₄ and C₂H₂ absorbing strongly in the 500-1000 cm⁻¹, 1300-1500 cm⁻¹ and 3200-2800 cm⁻¹ spectral regions.

In order to characterize the reaction products formed during the CH₄-H₂O photolysis at 3K we have analyzed the difference spectra before and after UV photolysis in 5 spectral regions:

→ ***C-O stretching region @ 1300-500 cm⁻¹***: this region corresponds to the torsion modes of many alka[e]nes and also to the C-O stretching mode of many alcohols. This spectral region is shown in figure 3 and it will be used to characterize the different alcohols formed under our experimental conditions.

→ ***H-C-H bending region @ 1500-1300 cm⁻¹***: this region shown in figure 4, corresponds to the bending modes of many alkanes and alcohols.

→ ***C=O functional group region @ 1900-1600 cm⁻¹***: this region shown in figure 5 corresponds to many species with C=O functional groups such as HCO and H₂CO. It will be used to characterize species with carbonyl functional groups which might be formed under our experimental conditions.

→ ***CO and CO₂ @ 2500-2100 cm⁻¹***: the region of CO and CO₂ molecules already shown in figure 2, will not be discussed as CO and CO₂ are natural reaction products from CH₄ oxidation.

→ ***CH and OH stretching mode region @ the 3500-2800***: This zone is dominated by the IR signals of (H₂O)_n, CH₄, C₂H₆ species and will be analyzed afterward during the heating of the sample, once all the alka[e]nes C_xH_y species, which desorb at temperatures lower than 80 K, are removed from the samples.

Figures 3 and 4 show the difference spectra before and after UV photolysis of CH₄-rich ices containing different amounts of water in the 1300-500 cm⁻¹ and 1500-1300 cm⁻¹ spectral regions, respectively. The analysis of the spectra from these two figures shows the formation of many alka[e]nes such as C₂H₆, C₂H₄, C₂H₂, C₃H₈ in addition to two radicals CH₃ and C₂H₅. The spectral positions of all these species are in good agreement with previous experimental^{4,5,14} studies devoted to CH₄ ice photolysis or radiolysis and showing that the

photolysis of methane leads mainly to the formation of saturated and unsaturated hydrocarbons. The adding of water into CH₄ ice shows, in the difference spectra, new IR features due to the formation of oxygen bearing species. As, the photolysis of methane ice leads mainly to long chain carbon species observed experimentally in figure 3 and as the adding of small amount water in methane ice brings additional reactants, during the photolysis of the sample, namely: H₂O, H, O, and OH species²², we can suggest that species with several carbon atoms and one oxygen atom may form first as primary reaction products. Consequently, CH₃ + OH, CH₃ + O, CH₂ + OH, CH₂ + O reactions may occur first leading to the formation of radical and stable species. In such a situation oxygen bearing species such as alcohols and aldehydes can be formed through processes involving fragments from methane and water. We notice from figure 3 that, counter to the IR signals of alka[e]nes whose spectral shapes and intensities are water independent, those corresponding to oxygen bearing species depend strongly in the amount of H₂O trapped in CH₄ matrix. In relatively diluted samples (figures 3a and 3b) the IR signals of the oxygenated photoproducts are clearly visible and well resolved. They become wider by increasing the water concentration in the sample (figure 3c). Accordingly, figures 3a and 3b allow the identification of oxygen bearing reaction products through their absorption bands which are clearly well defined and located at 1024.4, 1041.6, 1070.3, 1084.1, 1124.1, 1174.9, 1191.8, 1246.7 cm⁻¹.

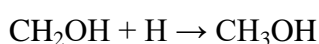
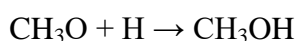
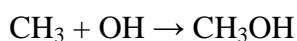
The C-O stretching absorption peaks of alcohols are intense and normally fall between 1200 and 1000 cm⁻¹. Consequently, the peaks at 1024.4, 1041.6, 1070.3 cm⁻¹ can be assigned to the C-O stretching mode of CH₃OH, CH₃CH₂OH, CH₃CH₂CH₂OH, respectively. The IR characterizations of solid CH₃OH, CH₃CH₂OH in different environments, have been investigated by many group. Moore and Hudson¹¹ for example measured the characteristic IR signal of CH₃OH and CH₃CH₂OH trapped in CH₄-H₂O ice at 1020 and 1047 cm⁻¹, respectively, which is in good agreement with our assignments, concerning methanol and ethanol.

It is important to notice that among those absorption peak which may correspond to photoproducts trapped in CH₄-H₂O environments, some would be due to hydrated complexes where a photoproduct is complexed to water such as CH₃OH-H₂O which are formed in samples with relative high amounts of water. This point will be discussed below concerning the H₂CO and H₂CO-H₂O detection. However, the matrix isolation study carried out by Bakkas et al²³ showed that the C-O stretching absorption peaks of CH₃OH is blue shifted by 13 cm⁻¹ in hydrated methanol. This suggests that under our experimental conditions CH₃OH-H₂O would absorb at 1033 cm⁻¹. Such a peak is not observed in figure 3a where the amount of water is

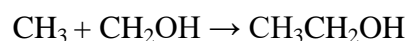
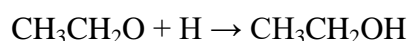
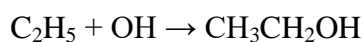
not high enough to form hydrated complexes. In the difference spectra of figures 3b and 3c a new peak appears at 1033 cm⁻¹, confirming the fact that hydrated complexes may be present under our experimental conditions only in samples with high amount of water (figures 3b and 3c). From these observations, we have checked systematically the absorption peaks related to the reaction products and those related to hydrated reaction products.

As mentioned earlier, the IR identification of CH₃OH and CH₃CH₂OH has been based on previous studies¹¹⁻²³, however, propanol has been less studied and for this reason, we have investigated the behavior of the spectral position shifts of the C-O stretching vibration of CH₃OH, CH₃CH₂OH and CH₃CH₂CH₂OH in solid phase. In fact, as it will be discussed below, we have measured the C-O stretching peaks positions of solid CH₃OH, CH₃CH₂OH, CH₃CH₂CH₂OH at 1023.8, 1045.7, 1067.9 cm⁻¹, respectively. This allows us to attribute the absorption peak at 1070.3 cm⁻¹ to propanol. The analysis to the IR intensities of these 3 peaks showed that these alcohols are formed with an IR intensity distribution CH₃OH: CH₃CH₂OH: CH₃CH₂CH₂OH = 10:4:1. The heating of the sample or the increasing of water amount in methane ice, as shown in figure 3c, lead to an overlapping of these three IR signals, resulting in a wide absorption band centered around 1035 cm⁻¹ and expanded between 1077 and 988 cm⁻¹. As the photolysis of CH₄ leads to the formation of long carbon chain species such as C₂H₆, and C₃H₈, naturally the adding of small amounts of water leads to the formation of the three alcohols we mentioned, probably through the subsequent mechanisms:

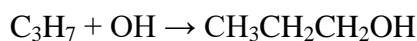
Formation of CH₃OH



Formation of CH₃CH₂OH



Formation of CH₃CH₂CH₂OH



Among all these mechanisms, those involving CH₃, C₂H₅, CH₃O and CH₂OH radicals are very probable as the four radicals have been observed experimentally under our experimental conditions. We have measured the spectral positions of CH₃ and C₂H₅ at 609.2 and 532.6 cm⁻¹, respectively, which is in good accordance with previous studies^{4,5,14} concerning the fragmentation of methane ice. Another band at 1385.3 cm⁻¹ (figure 4) behaves similarly as the bands at 609.2 and could also be due to the radical species CH₃. We have assigned, based on water concentration effects and sample heating, the peak at 1191.8 cm⁻¹ to CH₂OH radicals (figure 3). Previous experimental studies involving radiation induced processing of H₂CO and CH₃OH ices have shown the formation of CH₂OH through its most intense^{24,25} IR signal around 1190 cm⁻¹, while CH₃O, probably more reactive, has not been detected. The experimental observation of radicals would suggest that complex organic molecules other than CH₃OH, CH₃CH₂OH and CH₃CH₂CH₂OH may be formed through radical-radical recombination such as CH₃O + CH₃ to form CH₃OCH₃, CH₃O + CH₂OH to form CH₃OCH₂OH or CH₃O + CH₃O to form CH₃OOCH₃. The most intense IR signals characterizing CH₃OCH₃, CH₃OCH₂OH and CH₃OOCH₃, have been reported by several groups^{26,27} to be located at 1173, 1125 and 1032 cm⁻¹. We have observed under our experimental conditions two IR signals located at 1174.9 and 1124.1 cm⁻¹ which may be assigned to CH₃OCH₃ and CH₃OCH₂OH, respectively. We notice that the IR signals at 1174.9 cm⁻¹ characterizing CH₃OCH₃ is much higher than that at 1124.1 cm⁻¹, assigned to CH₃OOCH₃, indicating that species with one oxygen atom are probably formed more efficiently than species involving two oxygen atoms. CH₃OOCH₃ species cannot be experimentally characterized as its most intense IR signal at 1032 cm⁻¹ falls in the same spectral region as methanol and ethanol. Finally, the two peaks detected at 1246.7 and 1084.1 cm⁻¹ from figure 3 have been assigned to H₂CO and CH₂OHCH₂OH. These two species have been identified in irradiated CH₃OH and CH₄-CO ices^{28,29} at 1246 and 1088 cm⁻¹, respectively. In these previous studies H₂CO has been characterized by three characteristic absorption signals at 1726, 1499 and 1246 cm⁻¹. We also observe, under our experimental conditions these three signals at 1736.2, 1495.5 and 1246.7 cm⁻¹, as shown in figures 3, 4 and 5. These three peaks are assigned to H₂CO as they behave similarly when the sample is heated or when the CH₄ and H₂O concentrations change.

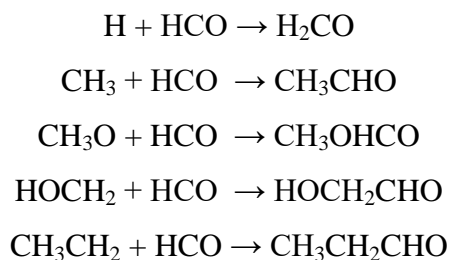
Figure 5 shows the spectral region for the C=O functional group in radical species such as HCO which absorbs around 1860 cm⁻¹ and stable molecules like the aldehydes H₂CO and CH₃CHO whose absorption bands are located around 1720 cm⁻¹. In this context Kaiser et al²⁹

investigated the irradiation of CH₄-CO ice to monitor the formation of complex organics with C=O group through the analysis of a wide absorption band detected at 1727 cm⁻¹. They showed, using a deconvolution of the observed C=O functional group absorption band, that irradiation of CH₄-CO ice may lead to the formation of HOCH₂CHO, CH₃CH₂CHO, H₂CO, CH₃CHO, CH₃OCHO which would absorb at 1743, 1746, 1727, 1726, 1714 cm⁻¹, respectively.

Figure 5 shows that, under our experimental conditions, the band corresponding to the C=O functional group depends strongly on the amount of water in CH₄ ice. It becomes wide and unresolved for samples with CH₄:H₂O concentration equal to 3:1 (figure 5c).

In the infrared spectra corresponding to the lowest concentration of water (figures 5a), as there is not enough water to form hydrated species at 3K, we distinguish three absorption peaks at 1756.4, 1736.2, 1726.4 cm⁻¹, which can be assigned to CH₂OHCHO, H₂CO, CH₃CHO, respectively. The identification of H₂CO and CH₃CHO is obvious as the peak at 1736.2 assigned to H₂CO correlates with other IR signals characteristic to H₂CO observed at 1495.5 and 1246.7 cm⁻¹ shown in figures 3 and 4. On the other hand, Kaiser et al showed that CH₃CHO trapped in methane ice²⁹ is characterized by its intense IR signal located at 1728 cm⁻¹. The peak detected at 1756.4 shows a vibration frequency higher than 1740 cm⁻¹ and it can be assigned to CH₂OHCHO. Bennett et al³⁰ reported the spectral position of CH₂OHCHO at 1757 cm⁻¹ in irradiated methanol-carbon monoxide ice experiment. Previous studies³¹ have reported the spectral positions of the C=O functional group in CH₂OHCHO ice at 1747 cm⁻¹. The peak observed at 1756.4 under our experimental conditions could also be due to aldehydes with alkyl groups (C_nH_{2n+1} with n > 1). In fact Kaiser et al²⁹ showed that saturated aldehydes with alkyl functional groups such as propanal (C₂H₅CHO) and butanal (C₃H₇CHO) trapped in CH₄ matrix show IR absorption signal with frequencies in the 1740-1750 cm⁻¹ range, while ketones with alkyl groups such as acetone (CH₃COCH₃) absorb in lower frequency range around 1717 cm⁻¹. We have recently reported³² the CO group spectral positions in CH₃CH₂CHO and CH₃OCHO ices at 1729 and 1711 cm⁻¹, respectively. This suggests that the peak observed at 1717.4 cm⁻¹ (figure 4b) would be due to either CH₃COCH₃ or CH₃OCHO. However we think that species with one oxygen are more probable under our experimental conditions. As shown in figures 5b and 5c, the signal at 1717.3 cm⁻¹ overlaps with the IR signal of the aldehydes trapped in samples with high amount of water and consequently part of this signal could be due to hydrated aldehydes. In figure 5c the wide absorption band due to the aldehydes interacting with water is centered at 1721.5 cm⁻¹ with a signal extended from 1800 cm⁻¹ to 1650 cm⁻¹. All these complex organic molecules formed

under our experimental conditions involve CHO fragment and might form through the following reactions:



Species such as H₂CO and CH₃CHO may be formed through processes such as H + HCO and H + CH₃CO which involve radical species with CO functional group. Many of these radical species absorb around 1860 cm⁻¹. The analysis of the IR signal in this spectral region shows that the absorption band is water concentration dependent. In figure 5b corresponding to a sample with relative high amount of water we distinguish 4 components located at 1858.8, 1849.4, 1842.4 and 1834.8 cm⁻¹. In samples with low concentration of water (figure 5a), we distinguish 2 absorption peaks at 1858.8 and 1849.4 cm⁻¹ while in figure 5c corresponding to samples with huge amount of water the observed band is wide and centered at 1846.1 cm⁻¹. All these IR signals located between 1860 and 1830 cm⁻¹ may be due to radical species such as HCO, CH₃CO, HOCO or to hydrated HCO. HCO has been measured at 1842 cm⁻¹ and 1846 cm⁻¹ in previous studies devoted to irradiation of H₂CO and CH₃OH ices^{28,33}, respectively. CH₃CO, HCO and HOCO trapped in argon matrix^{24,34} have been observed at 1875, 1864 and 1843 cm⁻¹, respectively.

As mentioned earlier, the goal of the present work is to have an IR spectrum of heavy oxygenated species which would be formed through the photo-induced solid state reaction involving H₂O and CH₄. Table 1 gathers a tentative assignment of species formed and trapped in methane ice at 3 K. The three spectral regions we have chosen to analyze are the only regions which are less perturbed by the IR signals of the reactants H₂O and CH₄ and the photoproducts proper to CH₄ fragmentation such as C₂H₆ which is formed efficiently under our experimental conditions. The 1500-1300 cm⁻¹ and 3020-2500 cm⁻¹ spectral regions, corresponding respectively to the CHC bending and CH stretching modes of many alcohols and alkanes, are dominated by the IR signal due to CH₄, C₂H₆ and C₂H₄ species which may hide the oxygen organics signals. In order to overcome such a problem we have heated the irradiated samples to be certain that all the alka[e]nes (C_xH_y) species are desorbed from our samples. It is important to notice that all alka[e]nes desorb at temperatures lower than 80 K

while the alcohols and aldehydes desorb at temperatures higher than 100K. We have then heated the irradiated CH₄-H₂O ices to 110K for a new IR analysis of our irradiated heated samples.

Table 1: Tentative assignments of the IR signals detected during the VUV Photolysis of CH₄-H₂O mixture at 3 K

<i>Spectral position (cm⁻¹)</i>			
Present work	Literature	References	Reaction product
1024.4	1020	11	CH ₃ OH
1033.0	1033	23	CH ₃ OH-H ₂ O
1041.6	1047	11	CH ₃ CH ₂ OH,
1070.3	1068	*	CH ₃ CH ₂ CH ₂ OH
1084.1	1088	28,29	CH ₂ OHCH ₂ OH
1124.1	1125	26,27	CH ₃ OCH ₂ OH
1174.9	1173	26,27	CH ₃ OCH ₃
1191.8	1190	24,25	CH ₂ OH
1246.7	1246	28,29	H ₂ CO
1495.5	1499	28,29	H ₂ CO
1717.4	1717	29	CH ₃ COCH ₃
1726.4	1728	29	CH ₃ CHO
1736.3	1726	28,29	H ₂ CO
1846.1	1846	28,33	HCO
1756.4	1757	30	CH ₂ OHCHO

* The C-O stretching peak IR position of solid CH₃CH₂CH₂OH has been measured in our lab.

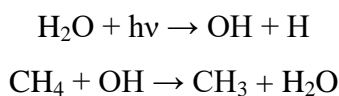
Figure 6 shows the results of the heating to 110 K of the irradiated methane rich ices containing different amount of water. As mentioned in the introduction part, all the laboratory simulations of energetic processing of CH₄-H₂O mixed ices, have been carried out in water rich environments in order to provide significant data correlating to observations. However such simulations cannot reveal the nature of all chemical species formed during the photo induced irradiation of CH₄-H₂O mixed ices. This is only because of the huge wide absorption bands of water ice which hide many reaction products. In order to avoid such a problem, we have to reduce the absorption signal due to water ice. The analysis of the IR spectra from figure 6 shows that even under our experimental conditions which use CH₄-rich ices with relative low concentration of water trapped in solid methane (figure 6a: 33 % of H₂O in CH₄, figure 6b: 17 % of H₂O in CH₄) the heating of the irradiated sample to 110 K to remove all alka[e]nes leads to wide absorption bands due to water ice where CH₄ and reaction products remain trapped in water ice (figures 6a and 6b). From these two figures, we can distinguish signals due to, C-O vibration of alcohols around 1000 cm⁻¹, to C=O functional group around 1700 cm⁻¹, and to HCH bending and C-H stretching modes of alcohols and alkanes around

1300 and 3000 cm⁻¹, respectively. Such conditions cannot help with indentifying the oxygen bearing species formed through CH₄+H₂O solid state photo-induced reaction. The situation is completely different when the very diluted samples (Figures 6c and 7a: 0.5 % of H₂O in CH₄) are heated to 110 K. The heating of such irradiated CH₄-H₂O ices allows to remove all alka[e]nes, including CH₄ and the IR signal due to H₂O ice is low enough to allow a better identification of the complex organic molecules formed through VUV photolysis of CH₄-H₂O. Figure 7 shows the IR spectra of the UV irradiated ice CH₄:H₂O (200 : 1) heated to 110 K, compared to the reference spectra of some organic molecules.

The IR spectrum of the heated irradiated methane-rich ice containing 0.5 % of water contains IR signatures characteristic of organic molecules having OH, CH, C=O and C-O functional groups. All the species we have proposed to form under our experimental conditions at 3K may fit the IR signatures of the resulting spectrum shown in figure 7a . The IR signal due to the C=O functional group is wide and it is located in 1790-1600 cm⁻¹ range cm⁻¹. It shows a maximum at 1725 cm⁻¹ with two components at 1750 and 1660 cm⁻¹. Due to the C=O functional group, many large aldehydes and even acids have intense IR signals in this spectral region. Similarly, the IR signal in the C-O stretching spectral region to characterize alcohols, is located in 1140-780 cm⁻¹ spectral range, showing a first maximum at 1027 cm⁻¹, and another one at 911 cm⁻¹. In the CH spectral region, we notice from figure 7a a structure of 6 peaks at 2971, 2963, 2958, 2934, 2874 and 2831cm⁻¹. Such a structure is indicative to the presence in the sample of alcohols larger than methanol and ethanol such as propanol. We have limited the comparison of the IR spectrum of the heated irradiated methane-rich ice to a few IR reference spectra of long chain carbon species containing one oxygen atom: CH₃OH, CH₃CH₂OH, CH₃CH₂CH₂OH, and CH₃CH₂CHO. The comparison of all these reference spectra to our experimental spectrum shows that in addition to small organics such as H₂CO, CH₃CHO, CH₃OH and CH₃CH₂OH already identified in previous CH₄-H₂O irradiation experiments, at least two large complex organic molecules such as propanal and propanol may be formed in icy mixtures containing water and methane and exposed to energetic sources. In previous experiments related to the irradiation of H₂O-CH₄ mixed ices in water-rich environments only CH₃OH, C₂H₅OH, H₂CO, CH₃CHO in addition to CO and CO₂ have been experimentally observed as oxygenated reaction products.

The formation of alcohols such as CH₃OH, CH₃CH₂OH, CH₃CH₂CH₂OH derived from the corresponding alkanes CH₄, C₂H₆ and C₃H₈ may take place through two different mechanisms involving either O or OH fragments. Consequently, the role of water into the chemical evolution of H₂O + CH₄ UV induced reaction depends on the water fragment involved in the

processing. Dissociated into H and OH, H₂O may play a catalytic role as for each water fragmentation, a regenerated H₂O may form through H abstraction reaction from methane as follows:



The CH₄ + OH reaction is exothermic with a very low activation energy³⁵. This shows that water present even as traces in methane ice may contribute indefinitely, through successive H₂O regeneration (CH₄ + OH → CH₃ + H₂O), into the chemical transformation of methane during and even after ice irradiation.

Water may also dissociate into H₂ + O and in such a situation atomic oxygen in its excited state O(¹D) would react with methane to form either CH₃OH and H₂CO through oxygen insertion reaction into C-H bond. The reaction is barrierless and highly exothermic³⁶ which allows the formation of both methanol and fragments from methanol such as H₂CO:

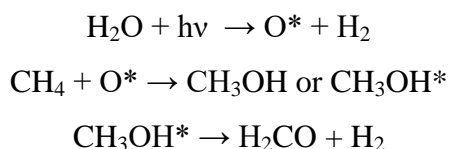
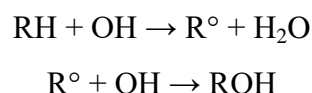


Figure 8 shows two energy diagrams involving OH + CH₄ and O(¹D) + CH₄ reactions, based on theoretical investigations carried out by Tsiouris et al³⁵ and Chang et al³⁶, respectively. Such processing involving either O and OH fragments from water and one methane molecule may be extended to all the hydrocarbons formed during the photolysis of CH₄ such as C₂H₆, C₂H₈ which react efficiently with OH through hydrogen abstraction reactions. Overend et al³⁷ measured in gas phase the rate constants of hydrogen abstraction from CH₄, C₂H₆ and C₃H₈ at 3.9 10⁹, 1.6 10¹¹ and 1.2 10¹² cm³ mol⁻¹ s⁻¹. Accordingly large linear alcohols involving radical alkyl, R : CH₃, C₂H₅, C₃H₈ may form through the following two steps reactions:



Conclusion

In the interstellar medium as well as in our solar system, the UV induced solid state chemistry of methane may be the source of many carbon chain complex organic molecules. As the chemical composition of many solar system and interstellar icy bodies are found to be dominated by H₂O, the photochemistry of methane has been investigated by several groups in water-rich ices in order to investigate, using IR spectroscopy, the oxygen bearing organics synthesis. Although these investigations are carried out to provide significant data correlating to the astronomical observations, they cannot reveal the nature of all the chemical species formed during the photo processing of CH₄-H₂O mixed ices. The huge wide absorption bands of water ice hiding many reaction products might be an hindrance to really characterize the CH₄ + H₂O photo-induced solid state reaction. We have shown in the present work the role played by water molecules in the photo-decomposition of solid methane and revealed that photoproducts formed in solid phase upon VUV irradiation of CH₄-H₂O mixture may be the source of very large complex molecules. The analysis of our IR spectra shows that the presence of water molecules even as traces in solid methane influences considerably its photochemistry at cryogenic temperatures. We show that in CH₄-rich environments both alka[e]nes such as C₂H₆, C₂H₄, C₂H₂, C₃H₈, CH₃ and C₂H₅ and large oxygen bearing organics such as H₂CO, CH₃CHO, CH₃CH₂CHO, CH₂OHCHO, CH₃OH, CH₃CH₂OH, CH₃OCH₃, CH₂OHCH₂OH are efficiently formed at temperatures as low as 3 K. However while the IR signatures of the alka[e]nes species C_xH_y dominate the IR spectra of the irradiated CH₄-H₂O ices at temperatures lower than 50K, the heating of the samples to 110 K reveals the formation of large carbon chain complex organic molecules having OH, CH, C=O and C-O functional groups and whose IR absorption signals are not perturbed nor shaded by the IR signals of water ice.

Acknowledgment

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Figure captions

Figure 1: IR spectra of CH₄-rich ices containing H₂O formed at 3 K with CH₄:H₂O concentrations equal to: a) 200 : 1, b) 6 : 1, c) 3 : 1.

Figure 2: IR spectra of CH₄-rich ices containing H₂O formed at 3 K, before and after UV photolysis. a) CH₄ + H₂O (200 : 1) ice, b) CH₄ + H₂O (200 : 1) ice after UV photolysis. c) CH₄ + H₂O (6 : 1) ice, d) CH₄ + H₂O (6 : 1) ice after UV photolysis. e) CH₄ + H₂O (3 : 1) ice, f) CH₄ + H₂O (3 : 1) ice after UV photolysis

Figure 3: Zoom in 1300-500 cm⁻¹ spectral region of the difference spectra before and after UV photolysis of CH₄-rich ices containing H₂O formed at 3 K, with CH₄:H₂O concentration equal to a) 200 : 1, b) 6 : 1, c) 3 : 1

Figure 4: Zoom in 1500-1300 cm⁻¹ spectral region of the difference spectra before and after UV photolysis of CH₄-rich ices containing H₂O formed at 3 K, with CH₄:H₂O concentration equal to a) 200 : 1, b) 6 : 1, c) 3 : 1. (*) not identified oxygenated species. The negative signal is due to CH₄ decrease during the ice photolysis.

Figure 5: Zoom in 1900-1650 cm⁻¹ spectral region of the difference spectra before and after UV photolysis of CH₄-rich ices containing H₂O formed at 3 K, with CH₄:H₂O concentration equal to a) 200 : 1, b) 6 : 1, c) 3 : 1. (*) band due to contributions from CH₃COCH₃, CH₃OCHO and hydrated aldehydes.

Figure 6: a) CH₄ + H₂O (3 : 1) ice after UV photolysis heated to 110 K. b) CH₄ + H₂O (6 : 1) ice after UV photolysis heated to 110 K. c) CH₄ + H₂O (200 : 1) ice after UV photolysis heated to 110 K. Top right: zoom of the figure in the 1200-800 cm⁻¹ spectral region.

Figure 7: a) CH₄ + H₂O (200 : 1) ice after UV photolysis heated to 110 K. Reference spectrum of solid b) CH₃CH₂CH₂OH c) CH₃OH, d) CH₃CH₂OH, d) solid CH₃CH₂CHO. Top right: zoom of the figure in the 3000-2600 cm⁻¹ spectral region.

Figure 8: Energy diagrams (kcal/mol) involving O(¹D) + CH₄ and OH + CH₄ reactions, based on theoretical investigations carried out by Chang et al³⁶ and Tsiouris et al³⁵. TS: transition states.

Figures

Figure 1

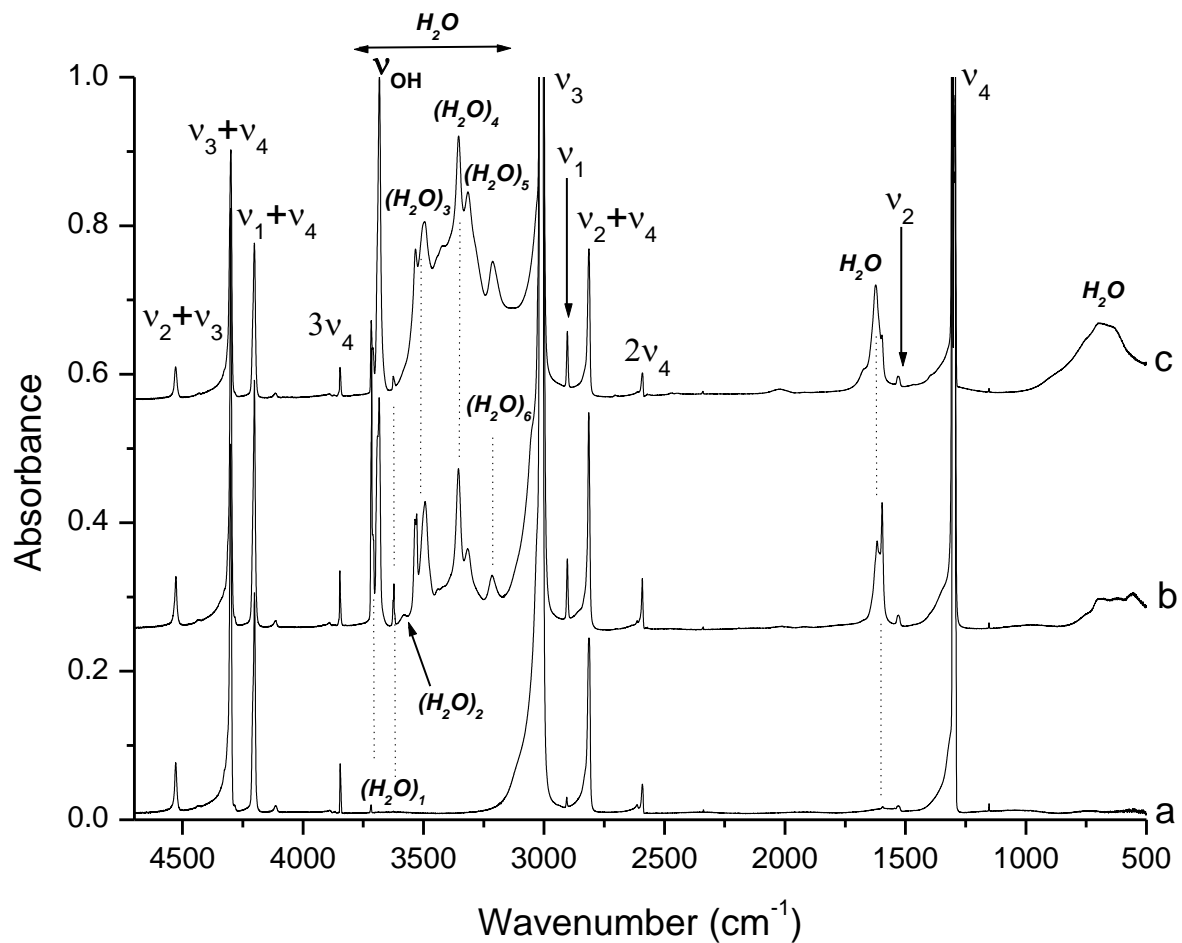


Figure 2

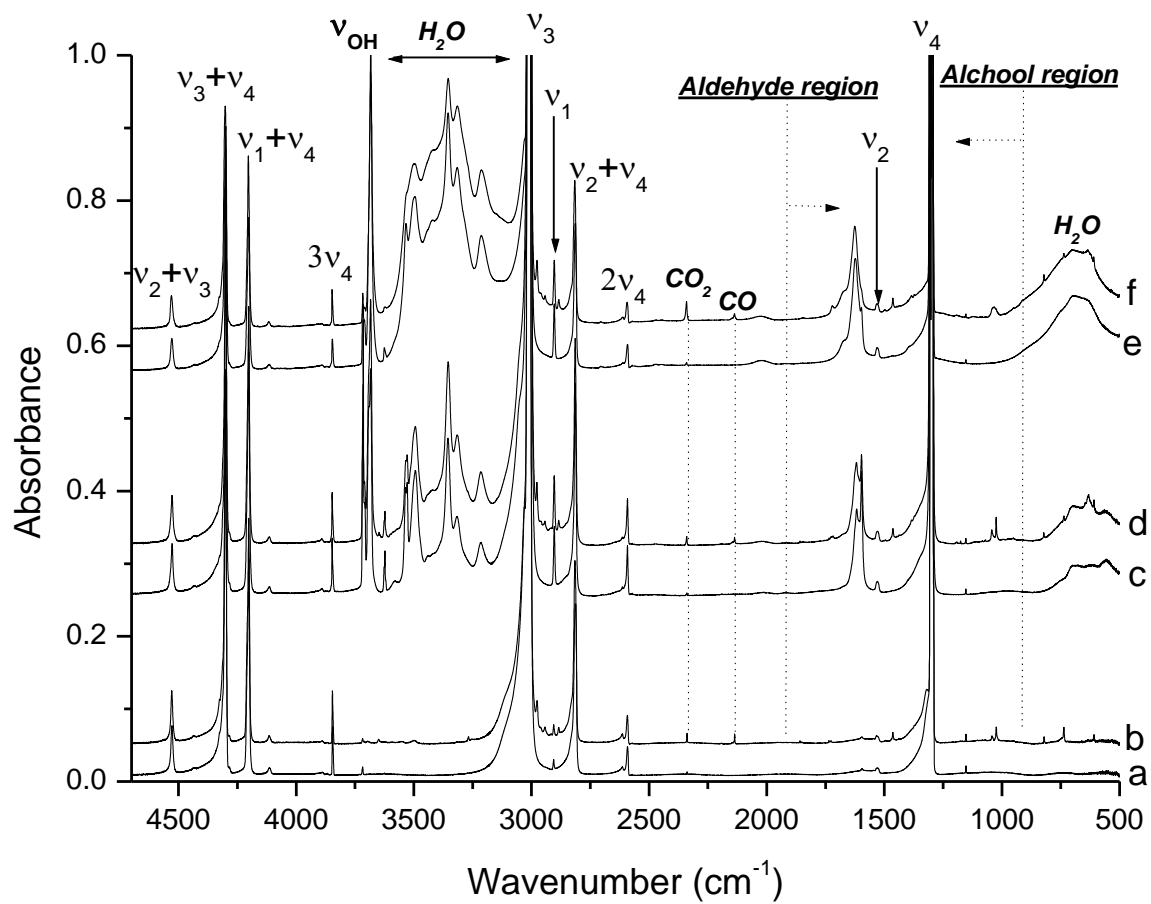


Figure 3

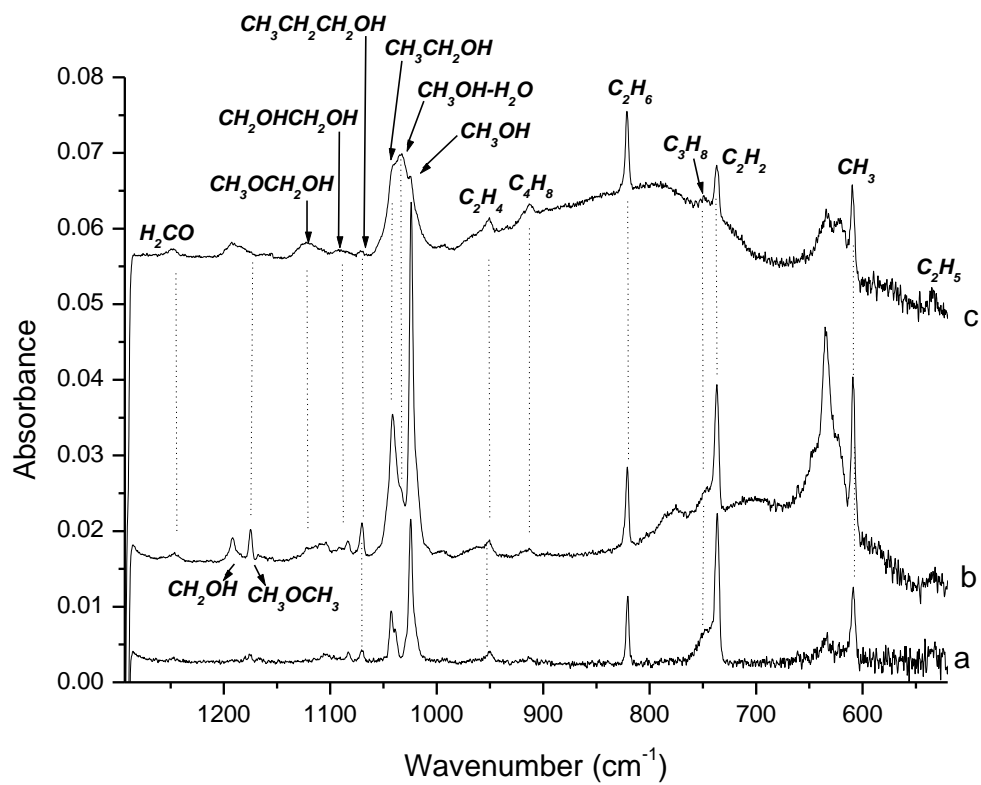


Figure 4

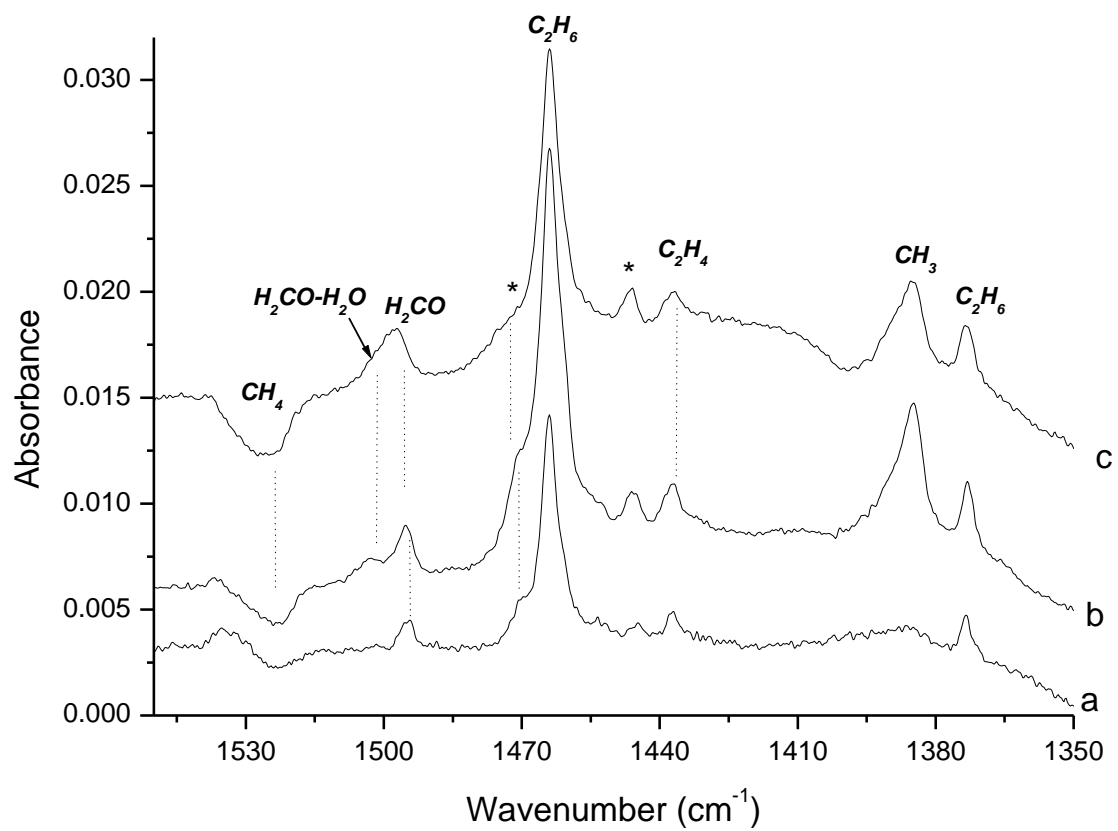


Figure 5

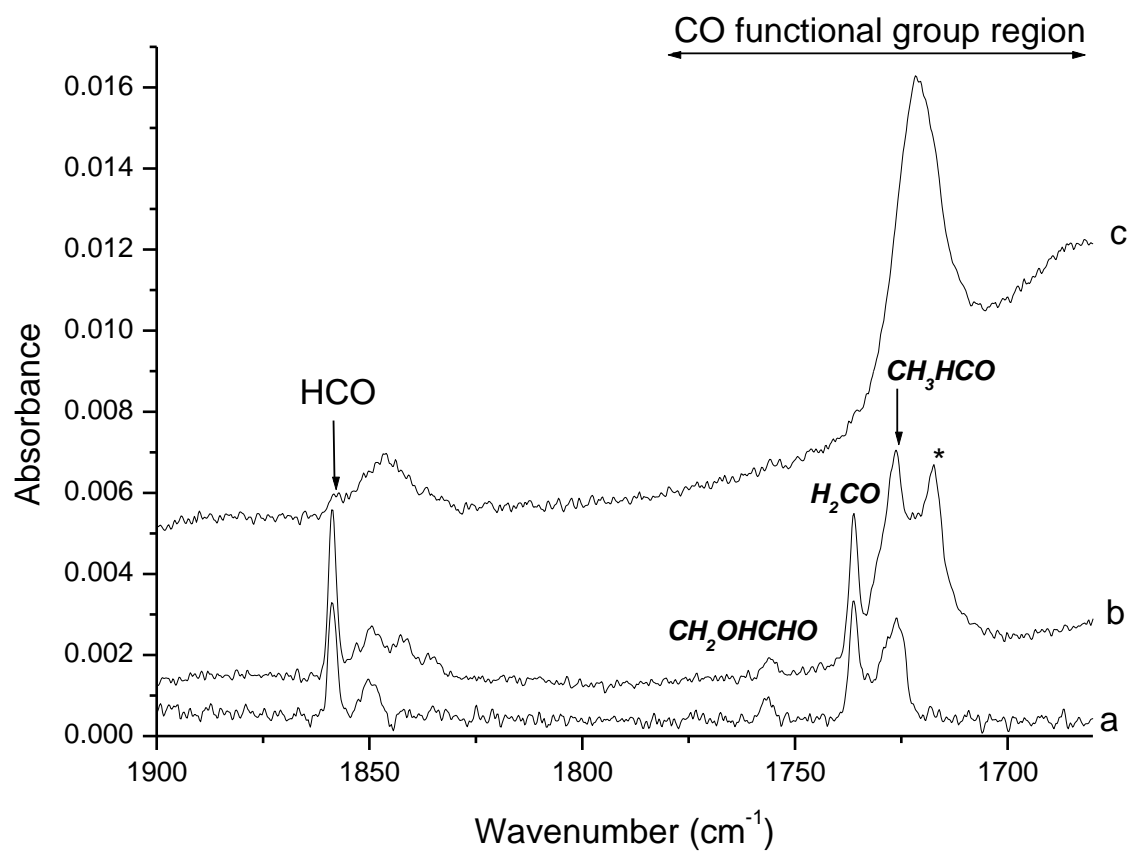


Figure 6:

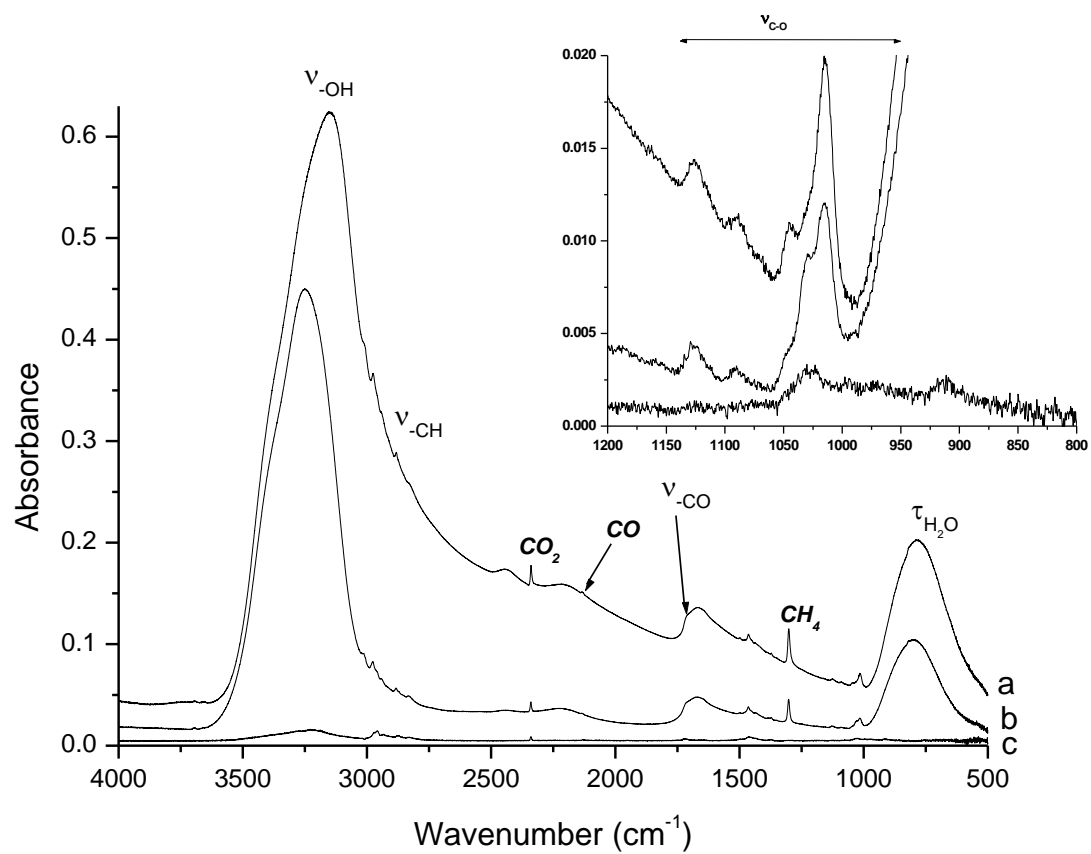


Figure 7

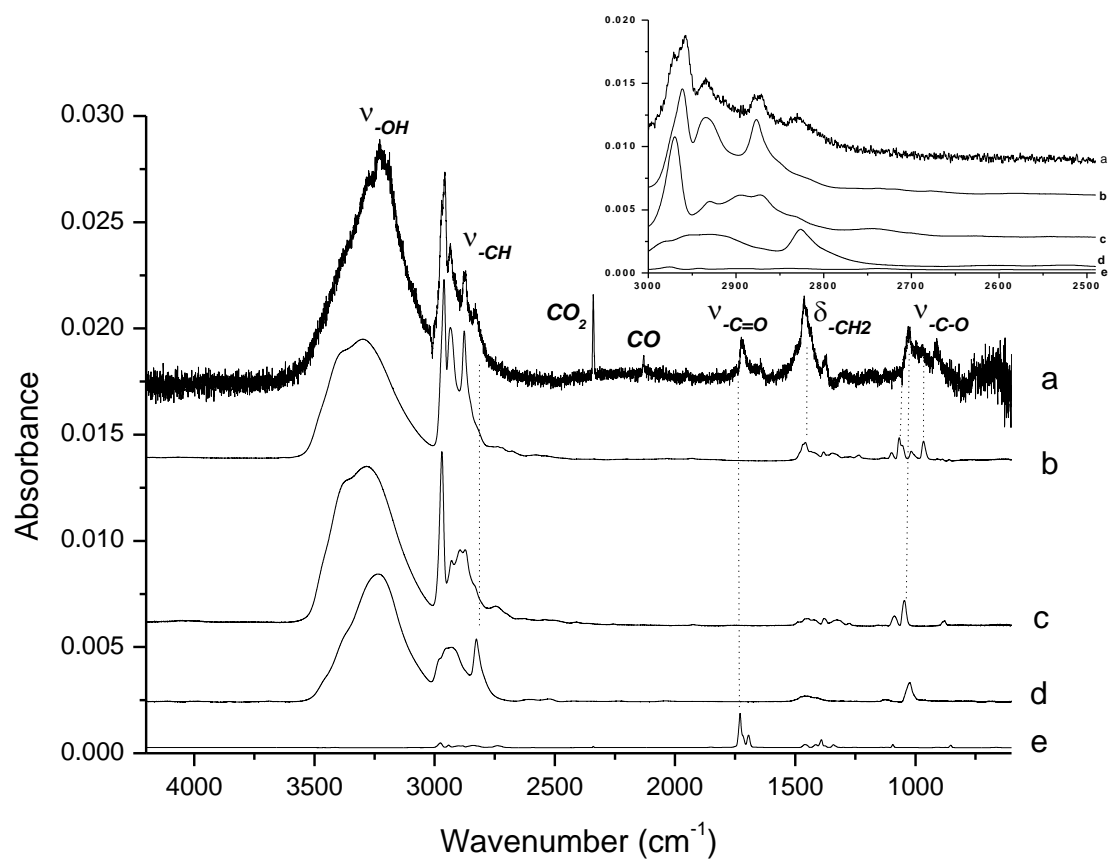


Figure 8

