



A temperature study of methanol interstellar ice analogues

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Summary

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Methanol ice has been studied in the field of astrochemistry for many years. As a simple organic compound, CH_3OH is extremely interesting in the study of ice formation and evolution. There are three forms of methanol ice – amorphous, α -crystalline, and β -crystalline. Although there are studies focused on the comparison of crystalline and amorphous phases in terms of chemical properties, there is a lack of systematic studies on phase transition. Factors such as pressure, temperature, and rate of ice formation have an influence on the process of phase transition. In this study, the influence of temperature on the vibrational properties of methanol ice is considered. For the experimental section, a Portable Astrochemistry Chamber (PAC) with the ability to control deposition pressure and temperature was used. The temperature of phase transition was experimentally determined at 103 K and for analysis of the ice structure, two vibrational modes were chosen – OH stretch and CH_3 in-plane rocking. Moreover, depositions at higher temperatures were performed with the result of different vibrational properties depending on ice formation conditions. This study presents the temperature-dependant properties of methanol ice in the mid-infrared spectrum and considers the possibility of thermal history determination.

Wpływ temperatury na metanolowe analogi lodu międzygwiazdowego (Streszczenie)

Słowa kluczowe:
analogi lodu
między-
gwiazdowego,
metanol,
krystalizacja lodu

Metanol w postaci lodu jest obiektem badań astrochemicznych od wielu lat. Jako prosty związek organiczny CH_3OH jest niezwykle interesujący w zakresie badań nad formowaniem i ewolucją lodu międzygwiazdowego. Wyróżnia się trzy formy stałe metanolu – lód w fazie amorficznej, α -krystalicznej oraz β -krystalicznej. Pomimo wielu badań nad porównaniem właściwości chemicznych metanolu w fazie amorficznej i krystalicznej widoczny jest brak systematycznych badań skupionych na przejściu fazowym. Czynniki takie jak ciśnienie,

temperatura czy tempo tworzenia lodu mają wpływ na proces przejścia fazowego. W ramach niniejszych badań rozpatrzono wpływ temperatury na spektroskopię oscylacyjną lodu metanolowego. W części eksperymentalnej wykorzystano przenośną komorę astrochemiczną (PAC) z możliwością kontroli temperatury oraz ciśnienia. Temperatura przejścia fazowego została eksperymentalnie oznaczona jako 103 K. Do analizy struktury badanego lodu wybrano dwa mody oscylacyjne metanolu – rozciągające OH oraz kołyszące w płaszczyźnie CH_3 . Co więcej, dokonano nanoszenia lodu w wyższych temperaturach, co zaskutkowało otrzymaniem odmiennych właściwości oscylacyjnych w zależności od warunków formowania lodu. Niniejsza praca przedstawia właściwości metanolu w formie lodu w funkcji temperatury w zakresie średniej podczerwieni oraz wskazuje na możliwość wyznaczania historii temperaturowej CH_3OH .

1. Introduction

Astrochemistry is an interdisciplinary field that relies on combined astronomical observations, computational modelling, and laboratory experiments. Experimental results are necessary for the interpretation and analysis of spectra gained from telescopes as well as for providing empirical input into astrochemical models. Moreover, new observational data, especially from the recently launched James Webb Space Telescope (JWST), will give an opportunity for a more detailed study of the chemical and physical properties of the icy particles in the Interstellar Medium (ISM) where molecules are formed. Chemistry in space is unlike the chemistry we are familiar with on Earth, and it is necessary to carefully mimic the conditions in space (extremes of temperature, pressure, and gravity forces) under controlled laboratory conditions. Therefore, comparing in-situ experimental results with observational data is extremely valuable.

Depending on the temperature region of the ISM, both gas-phase and solid chemistry are applicable. However, if to look at the star formation process and evolution of solar systems, the chemistry of interstellar dust and ice is crucial (van Dishoeck 2017). The largest reservoir of chemicals in the interstellar medium is in the form of icy mantles that coat microscopic carbonaceous/silicate particles in the dense molecular cloud regions of the ISM. Knowledge about the chemical and physical properties of solid-phase particles will better the understanding of the origin of complex molecules. The most abundant molecule in ISM's ice is H_2O . A combination of heterogeneous processes and the adsorption of molecules from the gas phase onto dust grains results in the growth of a solid mixture where other simple compounds such as CO , CO_2 , or NH_3 have been detected (Whittet et al. 1996). At some point in the evolution of the dense molecular cloud, gas phase CO accretes onto water ice, and methanol is formed via a successive hydrogenation process (Herbst and van Dishoeck 2009; Qasim et al. 2018). This results in the formation of layered ice

dominated by an H₂O-rich (polar phase) layer and a CO/CO₂-rich (non-polar phase) layer, with methanol in between (Papoular 2005; Garrod and Pauly 2011; James 2019). As a simple organic compound, CH₃OH is an interesting subject of study. When exposed to external radiation (e.g., cosmic rays, electrons, and ultraviolet photons), astrochemical reactions are initiated. This leads to the formation of new molecules, e.g., methane, glycol, or formaldehyde (Moore, Ferrante, and Nuth 1996; Schmidt, Swiderek and Bredehöft 2021) and gives an origin to organic chemistry under space conditions.

Although methanol's abundance varies greatly in different regions of space – from 4–17% in certain regions to 50–80% in other regions of ISM with respect to water (Palumbo, Castorina and Strazzulla 1999), an effective infrared (IR) analysis can be performed. With 12 vibrational modes, the methanol molecule is detectable in a wide spectral range (Moruzzi et al. 2018), enabling identification even when some of the bands overlap with other molecular absorptions. The most observed bands of solid methanol are at 3.53 μm (2832 cm⁻¹) and 9.7 μm (1030 cm⁻¹) which correspond to CH₃ symmetric stretch and CO stretch respectively (Gürtler et al. 2002; Pontoppidan et al. 2003). However, when focused on more bands in laboratory studies, their properties can also be identified. Solid methanol can occur in amorphous or crystalline forms depending on the temperature of the ice. There are two stable crystalline structures known for the methanol ice – α and β phase – with the temperature of transition at approximately 160 K (Torrie et al. 2002; Gálvez et al. 2009). An amorphous structure is formed at a lower temperature by vapor deposition. A crystalline structure is formed not only by deposition at a higher temperature but also by heating the amorphous phase. However, in the literature there are different values of phase transition temperature given: from 103 K (Torrie, Weng and Powell 1989; Dounce, Mundy and Dai 2007) to 128 K (Dempster and Zerbi 1971) and 133 K (Falk and Whalley 2004). This wide range of crystallisation temperatures implies the lack of detailed and comprehensive study in this field. What is more, not only temperature but also the pressure and thickness of ice could affect phase transition properties.

Despite research focused on methanol origin in ISM and its reactivity, there is a lack of systematic study on temperature-dependent ice structure. CH₃OH formation via hydrogenation is observed at the temperature of 20 K or below (Qasim et al. 2018). This solid-state mechanism leads to the formation of amorphous methanol ice. Moreover, CH₃OH molecules are scattered in CO₂ and H₂O ice, making it impossible to get a pure crystalline structure. However, methanol can be formed in the gas phase as well (Garrod et al. 2006; Wirström et al. 2011) leading to situations when vapours of CH₃OH can be deposited on the ice grain. Furthermore, desorption of methanol and re-adsorption can occur in the cycling of material in the temperature gradient around a protostar. Under those circumstances, it is worth considering the methanol ice structure depending on the temperature of deposition. Understanding the chemical

and physical properties of the different phases of methanol ice is therefore important in understanding the subsequent chemical pathways that lead to the formation of more complex organic molecules in star-forming regions.

From the authors' survey of the existing literature, studies considering the crystalline form of methanol ice are focused mainly on its reactivity, but not on the process of crystallisation. Comparisons of astrochemical reactions possible to detect in the amorphous and crystalline phase were performed with electron (Mifsud et al. 2022), ion (Palumbo, Castorina and Strazzulla 1999), or proton (Moore, Ferrante and Nuth 1996) irradiation. However, in all those cases, the crystalline phase was considered a constant structure that can be obtained by deposition at higher temperatures or by heating ice initially prepared at a temperature of approximately 20 K. Currently, there is no study focused on the dependence of crystallisation on the temperature of deposition. We believe that our study will help to better understand the influence of the temperature on the structure of methanol ice.

2. Experimental methodology

All the presented experiments were performed using The Open University Portable Astrochemistry Chamber (PAC) (James 2019) with the capability to achieve a base pressure of 10^{-9} mbar (Leybold TURBOVAC TMP 151 turbomolecular pump). Attached to a helium cryostat (Sumitomo DE-202B), Kapton flexible resistive heater (Omega), and temperature controller (Oxford Instruments Controller ITS 502), a base temperature of 20 K was attained by the substrate window in a spherical cube chamber. As a substrate for deposition, the ZnSe window was chosen for IR transmission. Liquid CH₃OH (Sigma-Aldrich >99.9% HPLC grade) was attached to the gas line and degassed with freeze-pump-thaw cycles. During deposition of the sample, temperature and pressure were set and controlled ensuring stable and repeatable conditions of the experiment.

The mid-IR analysis was performed in situ using a Fourier-Transform Infrared Spectroscopy (FT-IR) spectrometer (Nicolet Nexus 670) connected to an external Mercury Cadmium Telluride (MCT) detector. All spectra were measured in absorbance in a range of 4000–800 cm^{-1} at a resolution of 1 cm^{-1} . Both deposition and mid-IR analysis were carried out at an angle of 90° to the substrate, by turning the substrate accordingly to face the vapour deposition ports and the IR beam, respectively.

2.1. Low-temperature deposition

Methanol ice films were grown on the ZnSe window at a temperature of approximately 20 K. With controlled deposition pressure inside the chamber (1×10^{-6} mbar) and constant time of deposition (15 minutes), the amount of methanol used was similar in each experiment. After each deposition, FT-IR spectra were collected

to control the quality of deposition. The temperature of the substrate was then slowly and sequentially raised using the Proportional Integral Derivative (PID) function of the temperature controller at an average rate of 1 Ks^{-1} , with a slower step around the temperature of phase transition. While heating up, FT-IR spectra were collected, after every step of temperature change (depending on the phase of the experiment, steps were equal to 10, 5, 2 or 1 K).

2.2. Phase transition temperature deposition

After establishing that 103 K is the temperature of the phase transition, which agrees with Dounce, Mundy and Dai (2007), a series of experiments with a higher temperature of deposition was performed. Both the deposition rate and time of deposition were kept the same for all samples. For the data presented in this paper, temperatures of 98 K, 103 K, 108 K, and 113 K were chosen, and isothermal spectra were collected every 5 to 10 minutes until no changes were visible.

2.3. Rate of deposition and formation of layered ice

For the last set of experiments, a slower rate of deposition was chosen. With a deposition pressure of 1×10^{-7} mbar inside the chamber, the time of deposition was extended to 60 minutes. A temperature of 103 K was chosen as the point of phase transition. Then, having obtained crystalline-phase ice, the next layers of methanol were deposited with a pressure of 10^{-7} , 10^{-6} , and 10^{-5} mbar. The same experiment was then performed at a temperature of 21 K.

2.4. Thickness of the ice layer

The thickness of astrophysical ice analogues – d (μm) presented in Table 1 was estimated by using equation 1 (Mifsud et al. 2022):

$$d = 10^4 \frac{NZ}{N_A \rho} \quad (1)$$

where N_A is the Avogadro constant, which equals 6.022×10^{23} (molecules mol^{-1}), Z is the molar mass of methanol – 32 (g mol^{-1}), ρ is the mass density of the ice which was assumed as 0.64 (g cm^{-3}) for the amorphous phase and 0.84 (g cm^{-3}) for the crystalline phase (Luna et al. 2018). N – molecular column density (molecules cm^{-2}) was calculated by equation 2 (Mifsud et al. 2022):

$$N = \frac{P \ln(10)}{A_v} \quad (2)$$

Where A_v is the absolute band strength for C-O stretch mode equal to $1.61 (10^{-17} \text{ cm molecule}^{-1})$ for the amorphous phase and $1.18 (10^{-17} \text{ cm molecule}^{-1})$ for the crystalline phase (Luna et al. 2018), and P is the peak area of the analysed band (cm^{-1}).

Table 1. The thickness of chosen CH₃OH ice layers for amorphous and crystalline phases

CH ₃ OH phase	Temperature (K)	N ($10^{18} \text{ molecule cm}^{-2}$)	d (μm)
Amorphous	21.3	3.2	2.6
	21.2	3.2	2.6*
	20.7	3.1	2.5 #
	Average 2.57		
Crystalline	110.0	3.8	2.4*
	103.1	3.7	2.3 #
	103.0	3.8	2.4
	103.2	3.7	2.3
	Average 2.35		

Source: Own elaboration.

For the methanol ice layer grown at a low temperature, the average thickness was $2.57 \mu\text{m}$. Values from Table 1 show that with the same time and pressure of deposition, the resulting samples were of thickness comparable to each other. What is more, when methanol ice is in its crystalline form, the calculated value is smaller. Decreasing thickness is visible both when the phase transition was initiated by heating amorphous ice (marked with * and # respectively) and when methanol was deposited at a higher temperature. This can be caused by calculation error due to the uncertainty of the A_v values reported for the amorphous and crystalline phases (estimated 20% experimental error – Luna et al. 2018). However, the second possibility is a reduction of ice layer volume due to a more efficient spatial configuration of molecules in the crystalline structure and the creation of new hydrogen bonds (Baber et al. 2011).

3. Results and discussion

Ten vibrational modes of methanol were observed in all the infrared spectra. The band positions and their assignments are summarised in Table 2. After the phase transition, the peak maximum positions were shifted, which allowed the identification of crystalline ice formation. All the bands apart from the CO stretch were found to blueshift, and the most significant shifts were observed for ν_4 and ν_7 bands. Due to the sharpening of bands, the ν_2 and ν_9 modes, which were overlapped in the amorphous phase, split. The same splitting was also observed for ν_4 , ν_{10} , and ν_5 . Moreover, a wide band

of O-H stretch at 3247 cm^{-1} splits after phase transition into two new peaks with maxima at 3287 and 3179 cm^{-1} . For more detailed analysis, O-H stretch (ν_1) and CH_3 in-plane rocking (ν_7) was chosen due to the most visible changes in peak positions.

Table 2. List of absorption bands (cm^{-1}) characteristic of CH_3OH ice for amorphous and crystalline phases

Mode		Amorphous ice (21 K)	Crystalline ice (110 K)
OH stretch	ν_1	3247	3287, 3179
CH asymm. stretch	ν_2	2980	2985
CH asymm. stretch	ν_9	2955	2957
CH symm. stretch	ν_3	2828	2831
	$2\nu_8$	2036	2035
CH asymm. bending	ν_4	1475	1509
CH asymm. bending	ν_{10}	1460	1473
CH symm. bending	ν_5	1446	1455
CH_3 in-plane rocking	ν_7	1130	1143
CO stretch	ν_8	1028	1020

Source: Own elaboration.

3.1. The temperature of phase transition

While heating up the amorphous methanol ice, the first visible changes in the FT-IR spectra due to the phase transition were observed at the temperature of 103 K. After 110 minutes, no changes in the isothermal spectra were detected, which was interpreted as the completion of the crystallisation process. By collecting spectra in 10-minute time intervals, it was possible to observe the process of phase transition (Figure 1). The most significant change visible is the splitting of OH stretch mode into two components with increasing intensity of peak at 3287 cm^{-1} . Of particular interest is CH_3 in-plane rocking mode due to the new position, shifting from 1130 cm^{-1} to 1143 cm^{-1} and the shape-changing from a very broad band in the spectrum of the amorphous ice, to a much narrower, intense band in the crystalline sample (Figure 1 b). This change shows potential for using the ν_7 band as an indicator for discriminating between the amorphous and crystalline forms and possibly quantifying the contribution of each in any mixed phases.

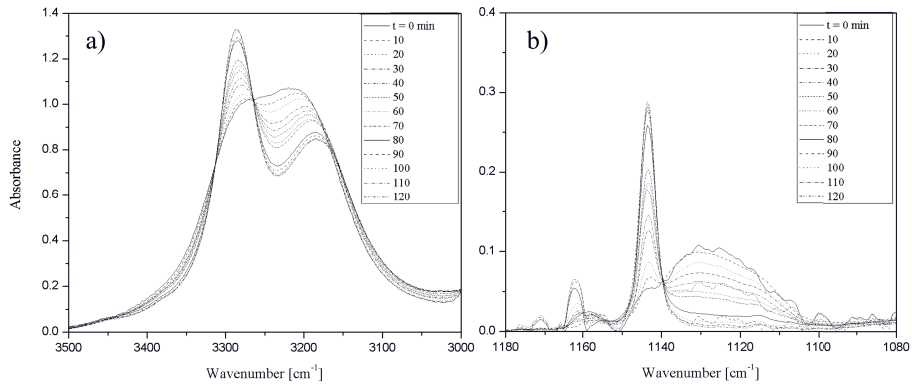


Figure 1. FT-IR spectra of CH_3OH ice layer initially deposited at 20 K and heated to 103 K. Spectra show isothermal phase transition at a temperature of 103 K: a) OH stretch; b) CH_3 in-plane rocking, collected in 10-minutes intervals for 120 minutes

Source: Own elaboration.

The lower temperature of phase transition observed in our samples in comparison with literature data could be due to differences in sample preparation conditions (e.g., pressure inside the chamber) and slower heating of the ice. For example, Dempster and Zerbi 1971, used conventional low-temperature cell without specifying the pressure or rate of deposition. Falk and Whalley, 2004, on the other hand, mentioned only using liquid nitrogen to freeze liquid methanol samples. However, at lower temperatures, the transition is slower which also could have an impact on experiment results. Without specific information about conditions of deposition, the thickness of the ice layer, and the time of isothermal measurements, it is hard to compare the temperature of crystallisation presented in the mentioned sources.

Upon heating of the amorphous CH_3OH ice, IR absorption bands have narrowed and some of the overlapped peaks have separated (Figure 2 a, b). Next to the CO stretch band, it was possible to observe a peak referring to the same mode but with respect to the ^{13}C isotope. Moreover, some new peaks appeared which have not been identified. Upon cooling down the crystalline methanol ice to 20 K (Figure 2 c), all the peaks except for ν_3 and ν_8 were found to blueshift slightly, which can be explained by the strengthening of the H-bonds (Góbi et al. 2020). In the case of CO stretch mode, when cooling down, the peak maxima is shifting to lower energies as was observed during crystallisation. The shape of the peaks did not change, which indicates that the crystalline form of methanol ice is stable and the transformation to the crystalline form is irreversible.

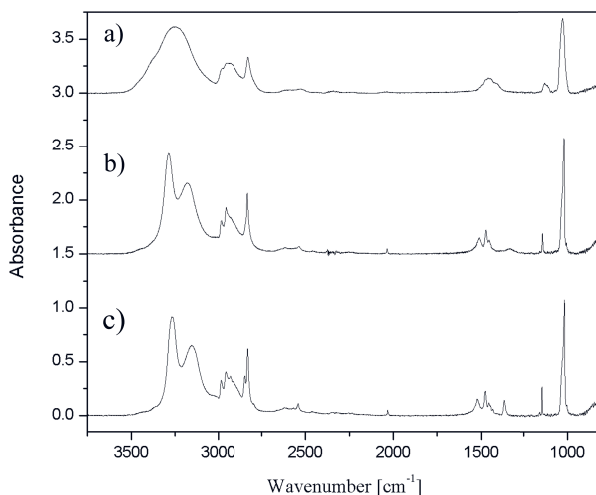


Figure 2. FT-IR spectra of CH_3OH ice layer: a) deposited at 20 K; b) heated up to 110 K; c) cooled down to 20 K after the phase transition. Spectra are offset vertically by 1.5 for clarity

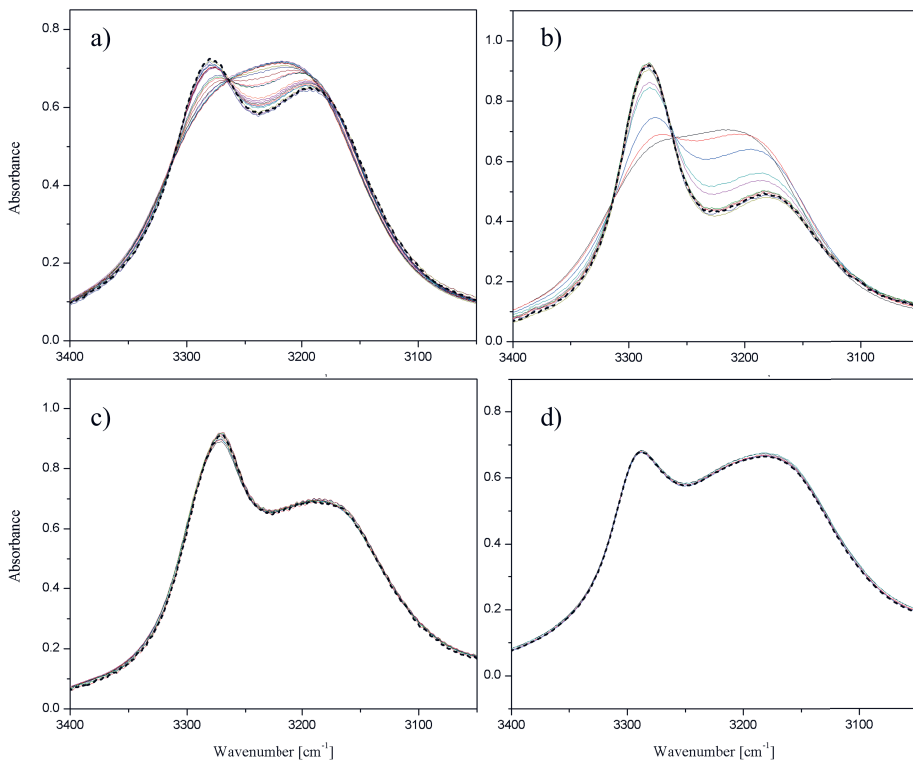
Source: Own elaboration.

3.2. The influence of temperature deposition on the methanol ice

We investigated the time taken for crystallisation to occur in the samples deposited at higher temperatures, close to the phase transition temperature. Depending on the temperature of deposition, different times of crystallisation were observed. For higher temperatures (108 K and 113 K) the crystalline structure was present already after deposition, but small changes in spectra were observed up to 160 minutes, which was interpreted as the end of phase transition. At the temperature of 103 K transition took 25 hours and at the temperature of 98 K changes in the spectra were visible up to 50 hours after ice formation. However, in the case of deposition at 98 K, although splitting of the OH stretch mode was observed, the CH_3 in-plane rocking band still contained a signal corresponding to the amorphous structure. Hence, changes at 98 K cannot be considered as full phase transition. This suggests, that even if some of the phase transition has taken place, not all the volume of an ice layer was in crystalline form.

Interestingly, each deposition temperature resulted in a slightly different final spectrum. The most significant change is visible while analysing the OH stretch band (Figure 3). The ratio between the two split components of this band is strongly dependent on the deposition temperature and it remains stable when the sample is cooled (Table 3). Interestingly, the ratio obtained for depositions at the temperature

of 98 and 113 K (1:0.90 and 1:0.98 respectively) is similar. However, when considering whole spectra properties, at the temperature of 98 K there is still an amorphous phase present in the ice layer which implies that OH stretch splitting is not fully developed. This result suggests that when focusing on the OH stretch band, this can tell us a lot about the thermal history of ice formation. A further detailed and systematic investigation is required to fully understand the influence of the deposition temperature and the crystallisation dynamics close to the temperature of the phase change. The observed difference also implies that while planning the next experiments including a crystalline phase of methanol ice, conditions of deposition should also be considered and whether the thickness of the ice also influences the crystallisation process.



Final spectra of crystalline CH_3OH ice are represented by the dashed line

Figure 3. Time-dependent FT-IR spectra of OH stretch mode of CH_3OH ice layer after deposition at: a) 98 K for 50 hours; b) 103 K for 25 hours; c) 108 K for 160 minutes; d) 113 K for 160 minutes

Source: Own elaboration.

Table 3. Comparison of crystallisation time and OH stretch mode properties for different temperatures of CH₃OH deposition

Temperature of deposition (K)	Time for complete crystallisation	Position of ν_1 mode peak (cm ⁻¹)	Ratio between the intensity of two components of ν_1 mode
98	50 h	3280, 3192	1:0.90
103	25 h	3282, 3183	1:0.54
108	160 min	3270, 3185	1:0.76
113	160 min	3288, 3184	1:0.98

Source: Own elaboration.

3.3. The influence of the rate of a deposition while obtaining the next layers of ice

While considering factors defining conditions of forming interstellar ice analogues, it is not merely the temperature that is important, but also the rate of deposition. All experiments described above were performed with the pressure of 10^{-6} mbar; however, when the rate of deposition was slowed ($p = 10^{-7}$ mbar), a quicker phase transition was observed. Comparing the time of the phase transition for ice deposited at 20 K and 103 K, it is observed that crystallisation is quicker when amorphous ice was formed at a lower temperature and then heated up – 110 minutes. However, when considering the same temperature of ice formation (103 K), but a different rate of deposition, a slower deposition rate allows more time for the molecules to rearrange on the surface before the next layer is grown. With a slower rate of deposition, crystallisation took 150 minutes, and with a quicker rate it took 25 hours. In all three cases, the final forms of the FT-IR spectrum were comparable to each other. All peak positions, shapes, and ratios were similar, which implies the presence of the same crystalline structure.

In another experiment, having initially formed the crystalline structure of the methanol ice ($p = 10^{-7}$ mbar, $T = 103$ K, $t = 60$ min), subsequent layers were deposited at different rates onto the first layer of ice, and CH₃ in-plane rocking bands were analysed in terms of amorphous structure presence. At the temperature of 103 K in the range of deposition pressure from 10^{-7} to 10^{-5} mbar, only the crystalline phase was observed (Figure 4 a). While performing the same experiment at a lower temperature – 20 K – the deposition caused the formation of new amorphous layers on crystalline ice film (Figure 4 b) which is visible as the appearance of the second, wide component of ν_1 band at 1130 cm⁻¹.

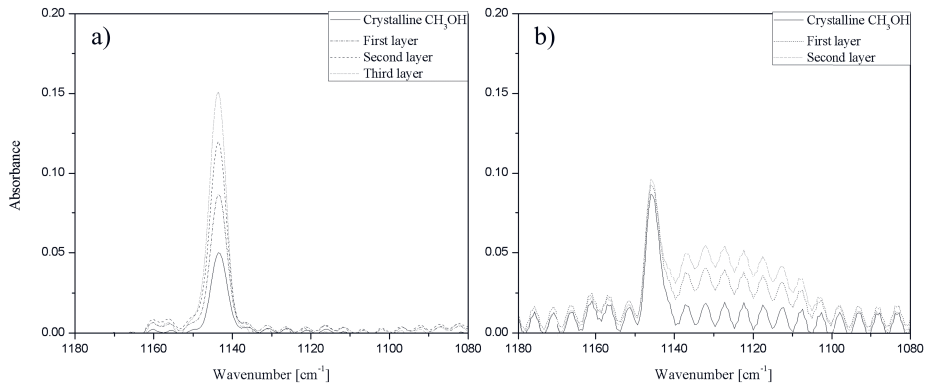


Figure 4. FT-IR spectra of CH_3 in-plane rocking mode of CH_3OH ice layers deposited on crystalline methanol at a temperature of: a) 103 K; b) 20 K. Deposition pressure: first layer – 10^{-7} mbar, second – 10^{-6} mbar, and third – 10^{-5} mbar. Fringes are observed in the baseline of the spectra due to wavelength-dependent interference at the interfaces of the ZnSe substrate. These become more pronounced due to the small thickness of deposited layers and lower signal intensity

Source: Own elaboration.

This result shows that the history of deposition has an influence on methanol ice structure. If only some stages of the ice formation took place at a higher temperature, it nevertheless is possible to detect the presence and fraction of both phases in the ice mixture.

4. Conclusion

The results presented in this paper show that conditions of ice crystallisation have an impact on the final structure of methanol ice. Differences in FT-IR spectra are visible especially when considering the deposition of CH_3OH at a temperature close to a phase transition. Also, the deposition rate has a significant influence on the crystallisation process. The slower the deposition rate, the faster the observed crystallisation rate is observed. However, the final ratio between ν_1 mode band components is the same for constant temperature of deposition despite differences in deposition rate. This suggests that the rate of ice formation has an influence only on the time of crystallisation but not on the vibrational properties of methanol ice, which is important information in the field of astrochemistry. The accretion rate in space is likely to be much slower rather than in laboratory timescales since the pressure in ISM is very low. However, experimental results having proved that the rate of deposition does not impact the structure of ice, it is more reliable to extrapolate laboratory data into astrochemical models.

Depending on the temperature of ice formation, different intensities of ν_1 mode band fractions can be observed. This shows the potential for further research concerned with the thermal history of methanol ice. With this knowledge, analysis of interstellar ice through interpretation of high resolution observational mid-IR spectra could provide more detailed information about the conditions of its formation and give clues about the interstellar environments in which the ices are formed. Moreover, the ν_7 mode band can be considered an indicator of amorphous phase presence in CH_3OH ice. The potential use of this band was shown experimentally while observing the formation of new layers of ice on pre-existing layers. The analysis of the CH_3 in-plane rocking band can be valuable while ice formation steps take place at different temperatures leading to the formation of a mixture of amorphous and crystalline phases, or when crystallisation is in progress.

Further research focused on methanol ice's properties as a function of temperature is required. A better understanding of the structure of the CH_3OH interstellar ice analogues in the case of different formation behaviour is crucial for the study of ISM history and evolution. Furthermore, investigating the chemical and physical properties of such methanol ices will be important to the understanding of the chemical evolution and formation of more complex molecules in star-forming regions of space.

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