INFRARED SPECTRA AND THERMODYNAMIC PROPERTIES OF CO₂/METHANOL ICES

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Received 2008 July 9; accepted 2008 September 4; published 2008 December 1

ABSTRACT

Ices of mixtures of carbon dioxide and methanol have been studied in a range of temperatures relevant for star-forming regions, comets, polar caps of planets and satellites, and other solar system bodies. We have performed temperature-programmed desorption measurements and recorded IR spectra of various types of samples. The presence of two slightly different structures of CO₂ is manifest. A distorted CO₂ structure is characterized by bandshifts between 5 cm⁻¹ (ν_3) and 10 cm⁻¹ (ν_2) with respect to normal CO₂. If the samples are heated above 130 K, the distorted CO₂ sublimates and only the normal structure remains. The latter can stay trapped until the sublimation of crystalline methanol (150 K). The desorption energy ($E_d \sim 20$ kJ mol⁻¹) of CO₂ from methanol ice, and the specific adsorption surface area (6 m² g⁻¹) of amorphous CH₃OH ice, have been determined. CO₂ does not penetrate into crystalline ice. Whereas the desorption energy is similar to that of CO₂/H₂O samples, the specific surface of methanol is much smaller than that of amorphous solid water (ASW). The interaction of CO₂ molecules with water and methanol is similar but ices of CH₃OH are much less porous than ASW. The inclusion of CO₂ into previously formed ices containing these two species would take place preferentially into ASW. However, in processes of simultaneous deposition, methanol ice can admit a larger amount of CO₂ than water ice. CO₂/CH₃OH ices formed by simultaneous deposition admit two orders of magnitude more CO₂ than sequentially deposited ices. These findings can have direct relevance to the interpretation of observations from protostellar environments (e.g., RAFGL7009S) and comet nuclei.

Key words: comets: general – methods: laboratory – molecular data – molecular processes – planets and satellites: general

1. INTRODUCTION

Observations in the near-infrared (NIR) and mid-infrared (mid-IR) spectral region have led to the identification of CO₂ and CH₃OH in the interstellar media and also in several solar system bodies. For example, measurements from the *Infrared Space Observatory* (ISO) have confirmed the co-existence of solid carbon dioxide and methanol in icy grain mantles in dense molecular clouds (e.g., Draine 2003; Gibb et al. 2004; Williams et al. 2007). CO₂ is the second most common component in interstellar icy grain mantles, with an average abundance of 17% with respect to water, the most abundant species. CH₃OH abundance on those mantles varies by an order of magnitude (3%–30%) between different sight lines (see Boogert & Ehrenfreund 2004). Depending on the ice formation history (e.g., increasing densities and molecular abundances as a function of time, or migration of grains in a turbulent cloud) different compositions or layer structures are observed in the grains. The rich chemistry of star-forming regions is largely determined by the evolution of the ice mantles with temperatures up to 200–300 K (Rodgers & Charnley 2003; Viti et al. 2004; Herbst 2005; Aikawa et al. 2008; Garrod et al. 2008), but the generation, thermal and chemical processing, and desorption of the various species in the ice layers are often poorly understood. In the envelopes of protostars, ices of CH₃OH and CO₂ can be formed through reactions of CO deposited on cold grain surfaces with hydrogen or oxygen atoms, respectively (Pontoppidan et al. 2004). This mechanism can be responsible for the depletion of a significant amount of CO. Spectral evidence for the observation of CO₂/CH₃OH complexes in circumstellar ices was discussed by Dartois et al. (1999; see also Klotz et al. 2004). Once formed, CO₂ and methanol should remain in the ice until they desorb to the gas phase in the higher temperature regions of protostellar cores (Aikawa et al. 2008). Current gas-grain chemical models

cannot yet justify the observed abundances of CO₂ and methanol (Garrod et al. 2008), but some predictions suggest that the relative proportion of methanol and CO₂ could be characteristic of different types of cores: CO₂ would be more abundant in isolated cores, whereas methanol and other organic molecules would prevail in cores embedded in ambient clouds (Aikawa et al. 2008). The coincidence of those two molecules has also been observed in comets (e.g., Bockélee-Morvan 1997). On the other hand, CO₂ has been observed in many satellites in our solar system (see e.g., the recent detection of CO₂ on Saturn's satellites Iapetus and Phoebe (Buratti et al. 2005), and in Jupiter's satellites Ganymede and Callisto, as inferred from reflectance spectra recorded by the Near-IR Mapping Spectrometer (NIMS) onboard the *Galileo* spacecraft (Carlson et al. 1996; McCord et al. 1998; Hibbits et al. 2002)).

Laboratory studies are essential to interpret the ice properties and thus to extract information about its formation history, as well as to allow modeling of these systems. The data required include, on the one hand, thermodynamic properties such as desorption temperatures and desorption enthalpies, binding energies, and specific surface areas, and, on the other hand, spectroscopic information such as band shapes and possible band shifts among different systems. Marked changes are observed in these two areas, thermodynamics and spectroscopy, when individual systems are compared to dual or more-component mixtures (Collings et al. 2004; Bar-Nun et al. 2007). The possibility of obtaining laboratory data in a wide range of temperatures offers an added value to the tasks of testing models and of comparison with observations from very different media.

The occurrence of solid methanol and CO₂ in different astrophysical bodies has motivated the study of this system using different techniques. Collings et al. (2004) and the group of Brown & Bolina (2007) and Bolina et al. (2005) have carried out an

extensive laboratory survey of astrophysical ices, using temperature-programmed desorption (TPD) techniques. They characterized the desorption of pure CO₂ and pure methanol from different substrates, although the methanol/CO₂ ice mixture was not analyzed. Several IR spectroscopy studies on methanol/CO₂ ices have been carried out in the last two decades (Ehrenfreund et al. 1998, 1999; Dartois et al. 1999; Kerkhof et al. 1999; Palumbo & Barata 2000; Bernstein et al. 2005). The works published between 1998 and 2000 dealt with methanol/CO₂/H₂O mixtures and were motivated mainly by *ISO* spectra taken in the line of sight of different IR sources, e.g., NGC 7538 and RAFGL7009S. In these observations, a triple band was present in the spectral region corresponding to the bending mode of CO₂, around 15 μ m. This peculiar band shape was attributed to the presence of an electron donor–acceptor (EDA) complex, with CO₂ being a Lewis acid and CH₃OH a Lewis base (Ehrenfreund et al. 1998, 1999; Dartois et al. 1999; Klotz et al. 2004). In the recent work of Bernstein et al. (2005), the binary system CH₃OH/CO₂ was explicitly surveyed. The mixtures were prepared by co-deposition of both gases in a bare substrate at 15 K. The evolution of the NIR spectra of these samples with increasing temperature was analyzed. The authors studied the variations in the spectrum of CO₂ in methanol with respect to the pure CO₂ spectrum. In particular they found the absorption at 4684 cm^{−1} to be thousands of times stronger in the mixtures than in pure CO₂. In addition, a recent *ab initio* study on H₂O–CO₂–CH₃OH complexes has appeared in the literature (Chaban et al. 2007). In that paper, theoretical spectra at MP2/aug-ccpVTZ level of the theory of the binary and ternary complexes are calculated, and the frequency shifts of the fundamental and first overtone vibrations of the complexes with respect to those of the monomers are discussed.

In this contribution we present an experimental study on CH₃OH/CO₂ ice mixtures by means of TPD experiments and IR spectroscopy. The objective of this research is to provide new and complementary data on a system of astrophysical interest that has not yet been sufficiently studied. The adsorption and diffusion processes that take place between methanol and CO₂ molecular ices are investigated in detail, revealing important differences between mixtures containing amorphous methanol or crystalline methanol, which could be formed if sufficient heating had been supplied to the ice. These differences affect also the IR spectra of the samples. Our investigation focuses on spectral changes apparent in the fundamentals and a combination band of CO₂, which can be related to astrophysical observations. We put forward a possible interpretation for such spectral variations in terms of the structure that carbon dioxide can adopt within the methanol ice.

Our samples are prepared by three different deposition schemes, and their behavior on heating is also investigated in a range of temperatures relevant for comets and solar system bodies. Since the process of formation of methanol or carbon dioxide in astrophysical ices is not yet well understood, the information provided by the different growing mechanisms of our systems, in sequential or co-deposition steps, may be relevant for the interpretation of observational data. Based on our TPD and spectral data, we can estimate desorption energies of CO₂ from amorphous and crystalline methanol, and also the amount of CO₂ embedded in the methanol bulk ice. The specific adsorption surface area of our methanol samples is determined as well. Moreover, a comparison of these results with previous studies on H₂O/CO₂ mixtures (Gálvez et al. 2007, 2008; Maté et al. 2008) provides an interesting view on the similarities and differences between these two systems.

2. EXPERIMENTAL SECTION

The experimental setup was described in detail before (Carrasco et al. 2002; Gálvez et al. 2008) and only a brief description will be given here. Solid samples of CO₂, CH₃OH, and mixtures of the two species were deposited from the vapor phase on a cold substrate located in a high-vacuum cylindrical chamber, evacuated by a turbomolecular pump. The temperature of the mounted substrate can be controlled, with about 1 K accuracy, between 80 and 250 K by means of a liquid nitrogen Dewar for cooling and a power transistor (2N3055) for heating. The background pressure in the chamber is usually below 10^{−7} mbar. The chamber is coupled to a Fourier transform IR (FTIR) spectrometer, Bruker Vertex70, through a purged pathway, with KBr windows for the incident and transmitted radiation, which is focused on exit onto a liquid-N₂ refrigerated MCT detector. In the transmission configuration used in this work, a 1 mm thick Si wafer was used as a substrate, situated on normal incidence to the incoming IR radiation. Spectra were recorded with a nominal resolution of 2 cm^{−1} (corresponding to about 0.5 cm mirror displacement in the interferometer), co-adding 512 scans for each spectrum. Controlled flows of CH₃OH (99.8%, from Scharlau) and CO₂ (99.998%, from Air Liquide) were admitted into the chamber through independent needle valves. The main chamber is coupled, by means of a regulation valve, to a differentially pumped chamber containing an Inficon, Transpector 2 quadrupole mass spectrometer (QMS). With this configuration the pressure in the QMS chamber can be maintained below 2 × 10^{−6} mbar for all the experimental conditions of the present work and the mass spectrometer can be safely used to check the purity of the species before each experiment, and to monitor the vapor composition during the deposition process. In all the experiments, the position of the regulation valve connecting the two chambers was kept fixed. This two-chamber scheme requires a careful calibration of the QMS—this was performed by correlating absolute pressure values of methanol or CO₂ in the main chamber, with the corresponding QMS readings at $m/q = 31$ and $m/q = 44$, respectively. The absolute pressure was determined from the growing rate of the solid films on the substrates (Maté et al. 2003). The film thickness values, needed for the calculation of the growing rate, were derived by simulating our transmission spectra with optical constants from the literature. In the case of methanol, the spectra were reproduced with the data of Hudgins et al. (1993). A sticking coefficient of 1 and a density of 1.013 g cm^{−3} were assumed at 80 K. The methanol density was derived from the 209.73 Å³ unit cell volume given by Torrie et al. (2002) for its α -phase. For CO₂ at 80 K, a sticking coefficient of 0.8 (Sandford & Allamandola 1990) and a density of 1.78 g cm^{−3} (Schulze & Abe 1980) were used. The optical constants of Ehrenfreund et al. (1997) were employed to simulate the IR spectra. These constants, which provide good agreement with the band intensities given by Gerakines et al. (1995), were selected because they allow the best simulation of our measured band profiles, but other sets of constants, sometimes with appreciable differences, are also available (Warren 1986; Baratta & Palumbo 1998). An additional calibration for CO₂, based on the relative electron impact ionization efficiencies of CH₃OH and CO₂ at the ionizer of the QMS was also performed. For an electron energy of 100 eV, values of 2.5 × 10^{−17} cm² (Tawara 1992) and 1.34 × 10^{−17} cm² (Viktor & Kurepa 1996) have been reported for the ionization cross sections of CO₂ and CH₃OH to yield mass fragments 44 and 31, respectively. The cross-section ratio was used to scale the QMS readings at the mentioned masses,

and hence to determine the CO_2 absolute pressure in the main chamber using the previous methanol calibration. An enrichment of the lighter species proportional to the ratio of the mean molecular velocities (~ 1.17) has been assumed in the flow through the valve between the deposition to the detection chamber. The two calibration methods were found to agree within 5%.

The calibration of the QMS remained stable in the course of the present experiments as verified by periodic checks. The estimated error in the absolute pressure values is $\sim 10\%$. Deposition pressures ranged between approximately 2×10^{-7} and 5×10^{-5} mbar.

Films of mixed $\text{CH}_3\text{OH}/\text{CO}_2$ ices were prepared by three types of deposition methods, equivalent to those used in our previous works on $\text{H}_2\text{O}/\text{CO}_2$ mixtures:

1. *Crystalline sequential deposition.* Methanol is first deposited at 85 K and then the temperature is raised to 130 K to induce crystallization (Torrie et al. 2002). The crystalline methanol film is subsequently cooled to 85 K and finally CO_2 is admitted.
2. *Amorphous sequential deposition.* Methanol is first deposited at 85 K and then CO_2 is added.
3. *Co-deposition.* Methanol and CO_2 are introduced into the chamber simultaneously, at the appropriate ratio, and deposited on the substrate at 85 K.

The column densities of methanol and CO_2 in the ice mixtures were calculated via the Lambert–Beer relation, using the integrated values of the IR absorption bands and the corresponding integrated absorption coefficients, A . For the ν_3 band of CO_2 , we used the value $A = 7.4 \times 10^{-17}$ cm/molecule, given by Gerakines et al. (1995), that corresponds to pure CO_2 ice at 100 K. For the methanol bands, we employed the value by Palumbo et al. (1999) for the 1026 cm^{-1} band of methanol at 10 K, $A = 1.3 \times 10^{-17}$ cm/molecule. In this case, we have determined a temperature correction factor of 0.97 using the spectra of Hudgins, recorded at 10 K and 75 K (see Figure 4 in Hudgins et al. 1993). With this correction, the A value at 75 K is 1.26×10^{-17} cm/molecule.

TPD experiments were performed by heating the substrate from 85 K to 180 K at constant rates of 0.3 K s^{-1} or 0.1 K s^{-1} , and monitoring the desorption of CO_2 and CH_3OH with the QMS. Most of the weakly bound CO_2 was desorbed at temperatures around 85 K–100 K. In this temperature interval, the CO_2 registered by the QMS comes from the substrate and also from other cold cryostat surfaces, which gives rise to an artificial broadening of the peaks. Since it is difficult to determine the origin of the desorbing molecules in this temperature range, we have focused our study on the region between 105 K and 180 K. The synchronization of the QMS with the heating ramps leads to an uncertainty of 1 K in the absolute temperature scale of the TPD figures.

3. RESULTS AND DISCUSSION

3.1. TPD Experiments

Desorption experiments on ice films generated by the three methods of deposition studied in this work are shown in Figure 1. The black and gray traces correspond to 31 and 44 amu, respectively (the dominant fragments in the mass spectra of CH_3OH and CO_2 , respectively). Sequential experiments (Figures 1(a) and 1(b) for amorphous and crystalline methanol, respectively) refer to methanol films with an approximate thick-

Figure 1. TPD graphs of $\text{CO}_2/\text{CH}_3\text{OH}$ ices grown in sequential or co-deposition processes as specified. The gray trace corresponds to QMS readings of 44 (CO_2); the black trace to QMS readings of 31 (CH_3OH). The CO_2 traces for sequential samples, (a) and (b), are scaled by a factor of 10.

ness of 300 nm deposited during 60 s with a CH_3OH pressure of 2×10^{-5} mbar, which were then exposed for 60 s to a CO_2 vapor dose at $p_{\text{CO}_2} = 4.3 \times 10^{-6}$ mbar. For the co-deposition experiment (Figure 1(c)), the same partial pressures of methanol and CO_2 as above were introduced during 60 s in the deposition chamber, but simultaneously.

In all three experiments the TPD trace of methanol exhibits a single peak at 165 K. The adsorption of methanol on various surfaces has been extensively studied due to its relevance in catalytic and astrophysical processes (see for instance Collings et al. 2004; Bolina et al. 2005 and the references cited therein). In the present experiments the observed peak corresponds to multilayer desorption and the range of desorption temperatures is related to the sublimation energy of solid methanol. However, the precise location and shape of the peak also depend on the experimental conditions, in particular on the film thickness and heating rate as discussed elsewhere (Collings et al. 2004; Bolina et al. 2005; Gálvez et al. 2007).

As indicated above, most CO_2 sublimates from various cryostat surfaces are below 105 K; this fraction is not considered here. CO_2 desorption in the 105–180 K temperature range shows different patterns for the different deposition schemes. In Figure 1(a), the TPD curve corresponding to the amorphous sequential mixture shows a weak feature for mass 44 at ~ 120 K, close to the temperature of the phase transition from amorphous to crystalline methanol (Dempster & Zerbi 1971). This desorption pattern indicates that part of the CO_2 molecules remain bonded to the amorphous methanol until it crystallizes, and then most of them suddenly leave the solid in a so-called “volcano desorption” process (Smith et al. 1997) during the major molecular rearrangement associated with the phase transition. In addition, a small feature at 150 K is observed, which coincides with the beginning of methanol desorption.

Figure 2. TPD graphs of CO₂/CH₃OH ices grown by co-deposition of the gases at the specified pressure ratios. As in Figure 1, the gray trace corresponds to QMS readings of 44 (CO₂); the black trace to QMS readings of 31 (CH₃OH).

In co-deposition experiments, the same peaks at 120 K and 150 K appear for mass 44, but with higher intensities than in sequential mixtures, which indicates that a larger amount of CO₂ remains in co-deposited samples above 105 K. The relative intensity of the two desorption peaks depends on the CO₂/CH₃OH partial pressure ratio during deposition, yielding a higher 150 K/130 K peak area ratio for higher CO₂ proportion in the gas phase. Two examples, at pressure ratios 0.3 and 1, are presented in Figure 2. In further experiments it was also observed that the amount of CO₂ that remains trapped in the ice mixture after methanol crystallization at 130 K depends on the heating rate employed to induce the phase change. We have carried out two experiments, heating ices of the same composition, from 85 K to 180 K, at 0.3 K s⁻¹ and at 0.1 K s⁻¹; we have observed that larger amounts of CO₂ are released at the faster heating rate. A possible explanation for this finding could be related to a sudden fracture of amorphous structures where CO₂ was occluded in the former case, as compared to a more gentle breaking at the slower heating pace. These observations will be discussed in the following section together with the corresponding FTIR spectra.

In crystalline sequential samples all the CO₂ was desorbed at $T < 105$ K, and consequently no variation of mass 44 was observed in the QMS (see Figure 1(b)). This behavior denotes that CO₂ molecules adsorbed on crystalline methanol do not enter into the methanol ice but form an external layer that desorbs similarly to pure CO₂ molecules on an inert substrate.

3.2. FTIR Spectra

3.2.1 Methanol

In Figure 3 we present transmission IR spectra of the crystalline and amorphous phases of methanol and of a CO₂/CH₃OH mixture prepared by co-deposition at 85 K. All the spectra presented in this paper are given in absorbance units, with $A = \log(1/T)$, recorded at normal incidence (i.e., 90° geometry) of

Figure 3. IR spectra of pure crystalline methanol, amorphous methanol, and a co-deposited mixture of CO₂/CH₃OH, bottom to top. All spectra recorded at 85 K. The two upper spectra are offset in the absorbance scale for clarity.

the unpolarized radiation on the cold plate. A spectrum similar to that of the co-deposited sample, at this level of detail, is obtained for sequential deposition and is not displayed in the figure. The inclusion of CO₂ does not originate any changes in the positions and relative intensities of the methanol bands in the ice mixture as compared with pure amorphous methanol ice. In general terms, our spectra show a good correlation with previous works, although in some cases the assignment is uncertain. As expected, crystalline samples present sharper bands than amorphous ones and multicomponent peaks appear in a number of spectral regions.

Two stable crystalline phases of solid methanol have clearly been evidenced (Parks 1925): the α -phase, stable below $T \sim 155$ K, and the β -phase, stable between ~ 165 K and the triple point at ~ 175.6 K. Both structures were characterized early by X-ray diffraction techniques (Tauer & Lipscomb 1952). The transition between the α and β phases has a very large hysteresis (Torrie et al. 2002), with possible mixtures of the phases co-existing at several temperatures. In addition, a metastable phase has been found to exist, between 130 and 145 K (Lucas et al. 2005). The full understanding of the phase situation of solid methanol is currently under study. Our spectrum of crystalline methanol is very similar to that assigned to the metastable phase by Lucas et al (2005) (see Figure 3 in Lucas et al. 2005). These authors formed this phase by condensation in the 130–145 K temperature range. Our crystalline phase was obtained by vapor deposition at 85 K followed by heating of the sample to 130 K, keeping the pressure at $\sim 10^{-7}$ mbar. Although the generating methods are different, they seem to lead to the same methanol phase judging by the matching of their corresponding IR spectra.

3.2.2 Sequentially Deposited CO₂/CH₃OH Ice Mixtures

The main IR absorptions of CO₂ in CO₂/CH₃OH ices generated by crystalline sequential and amorphous sequential deposition methods, at 85 K, are displayed in Figure 4, where the bands of pure CO₂ are also included for reference. The spectra of CO₂ sequentially deposited on crystalline and amorphous methanol films are very similar and the differences

Figure 4. IR spectra of sequentially deposited mixtures of $\text{CO}_2/\text{CH}_3\text{OH}$ in the most interesting spectral regions for the CO_2 vibrations. (a) ν_3 region, $\sim 2340\text{ cm}^{-1}$; the ν_3 band of the ^{13}C isotopomer can be seen at 2283 cm^{-1} ; (b) ν_2 region; (c) $\nu_1 + \nu_3$ region. The spectrum of pure CO_2 is also plotted for reference. Gray trace: CO_2 on crystalline methanol ice; black trace: CO_2 on amorphous methanol ice; dotted trace: pure CO_2 . All spectra are offset in the absorbance scale for clarity.

between these spectra and the spectrum of pure CO_2 are small. Ice mixtures in Figure 4(a) present the ν_3 band centered at 2350 cm^{-1} and a high frequency tail that ends in a second peak at 2372 cm^{-1} , somewhat more marked in crystalline sequential samples. The ν_3 bands of CO_2 in these $\text{CH}_3\text{OH}/\text{CO}_2$ mixtures are broader and slightly distorted with respect to the same band in pure CO_2 . This band of the ^{13}C isotopomer appears in all three cases as a single peak at 2284 cm^{-1} , barely appreciable at the right of Figure 4(a). Figures 4(b) and 4(c) show that the ν_2 and $\nu_1 + \nu_3$ bands, respectively, of CO_2 deposited on crystalline and amorphous methanol ices are similar to the same bands in pure CO_2 . These resemblances support the idea that CO_2 on sequential samples at this temperature forms a layer on top of the methanol ice, with similar characteristics to those of a pure CO_2 amorphous solid.

Figure 5 shows the temperature evolution of the ν_3 band of CO_2 deposited on an amorphous methanol film, heated from 85 K to 130 K at 0.3 K s^{-1} rate. Only a small peak centered at 2340 cm^{-1} remains at 105 K, and this peak disappears completely when the sample is annealed to 130 K. This behavior will be discussed below when dealing with co-deposited samples. On the other hand, no trace of the ν_3 band of CO_2 is present after warming at 105 K when carbon dioxide is deposited on crystalline methanol samples (not shown in the figure), as expected from the TPD measurements (see Section 3.1).

We are not aware of any previous literature data on sequentially deposited $\text{CO}_2/\text{CH}_3\text{OH}$ ices. We can conclude from our

Figure 5. IR spectra of a sequentially deposited mixture of $\text{CO}_2/\text{CH}_3\text{OH}$. The evolution of the spectra with increasing temperature is well appreciated in the ν_3 region.

TPD and FTIR transmission studies that in these systems most of the CO_2 is placed as a layer on top of the methanol film and evaporates when the sublimation temperature of pure CO_2 is reached. However, in amorphous sequential samples a fraction of CO_2 remains after heating above 100 K, giving rise to an absorption band at 2340 cm^{-1} and a TPD peak at 120 K. The shift in frequency with respect to pure carbon dioxide indicates a slightly altered structure of the molecule. These CO_2 molecules can be expected to stay inside the pores and canals of the amorphous methanol samples. An estimation of the amount of CO_2 adsorbed on amorphous methanol is discussed in Section 3.3. On the other hand, crystalline methanol ices are much less porous and consequently no CO_2 remains at $T > 100\text{ K}$.

3.2.3. Co-Deposited $\text{CO}_2/\text{CH}_3\text{OH}$ Ice Mixtures

Co-deposited ices of $\text{CO}_2/\text{CH}_3\text{OH}$ have been generated by vapor deposition at 85 K using different $p_{\text{CO}_2}/p_{\text{CH}_3\text{OH}}$ pressure ratios. The ice mixtures have been heated to 130 K at 0.3 K s^{-1} . Figure 6 displays our results on the IR spectra of co-deposited samples in four vertical panels corresponding to the spectral regions of the ν_3 band of $^{12}\text{CO}_2$, the ν_3 band of $^{13}\text{CO}_2$, the ν_2 band, and the $\nu_1 + \nu_3$ band. The spectra on the right-hand side were obtained for a highly concentrated mixture, with 63% carbon dioxide in the solid phase, formed at a vapor pressure ratio $p_{\text{CO}_2}/p_{\text{CH}_3\text{OH}} = 0.68$, and those on the left column correspond to a low-concentration mixture, with 8% CO_2 (solid) and $p_{\text{CO}_2}/p_{\text{CH}_3\text{OH}} = 0.15$ (gas phase). To study the variation of the mixtures with temperature, traces are shown for spectra at 85 K (black) and at 130 K (gray). To all the windows the corresponding spectrum of pure CO_2 ice at 85 K has been added for comparison.

The spectra of the larger CO_2 concentration samples at 85 K (right column) present in all cases a multiple structure, which appears to be composed of the peaks characteristic of pure CO_2 , plus adjoining red-shifted features. After heating to 130 K, most of the CO_2 is evaporated, but a small fraction remains showing only peaks at frequencies matching the pure CO_2 spectra. This reveals a dual structure of CO_2 in these samples, with a fraction of the molecules differing from the pure CO_2 solid. Interestingly, the lower CO_2 concentration samples at 85 K (left column) consist of only this distorted CO_2 , in a smaller proportion than in their concentrated counterparts, and which again evaporates from the samples on heating.

We may label the two different CO_2 structures as “normal” (norm) and “distorted” (dist), corresponding respectively

Figure 6. Left column: IR spectra of co-deposited CO₂/CH₃OH samples of low-CO₂ concentration ($p_{\text{CO}_2}/p_{\text{CH}_3\text{OH}} = 0.15$); right column: high-CO₂ concentration ($p_{\text{CO}_2}/p_{\text{CH}_3\text{OH}} = 0.68$). The spectral regions represented correspond, top to bottom, to the ν_3 band of ¹²CO₂, the ν_3 band of ¹³CO₂, the ν_2 band, and the $\nu_1 + \nu_3$ band. Black trace: spectra recorded at 85 K; gray trace: spectra recorded at 130 K; dotted trace: spectra of pure CO₂, added for comparison. All spectra are offset in the absorbance scale for clarity.

to that which is more similar to pure CO₂, or to that presenting a slightly modified structure characterized by red-shifted vibrational frequencies, which must arise from a direct interaction with methanol molecules. This latter structure should correspond to the CO₂–CH₃OH complex suggested by Dartois et al. (1999; see also Klotz et al. 2004), as the spectra of the mixture shown in Figure 5 of Dartois et al. (1999) in the 70–90 K range are very close to our traces recorded at 85 K (see especially Figures 6(d) and 6(f)). Moreover, our spectra could be compared with the observed trace of the sources RAFGL7009S and S140, and with the spectrum SWS06 of NGC 7538 IRS9, obtained by de Graauw et al. (1996), and reproduced also by Dartois et al. (1999). In previous works on CO₂/H₂O ices, these two CO₂ structures were referred to as “external” and “internal” respectively (Maté et al. 2008; Gálvez et al. 2007), but the present proposal seems more adequate, since the superficiality of the carbon dioxide molecules is not so evident for the methanol mixtures.

Our experiments reveal that CO₂ dist is always present in co-deposited CO₂/methanol samples at 85 K, with a concentration that grows with the $p_{\text{CO}_2}/p_{\text{CH}_3\text{OH}}$ ratio. Above a certain value of this pressure ratio, the CO₂ norm starts condensing and its proportion with respect to CO₂ dist rises with increasing $p_{\text{CO}_2}/p_{\text{CH}_3\text{OH}}$.

The band centers for the main vibrations of CO₂ dist recorded in the present experiments with co-deposited samples are listed in Table 1, together with pure CO₂ frequencies and compared with values from previous works. All results agree well, although the generation temperatures of the ices were different (85 K in our case, and much lower temperatures, 15 K or 10 K, in previous reports).

Our study of the evolution of the co-deposited ice mixtures with temperature ranged from deposition at 85 K to that of methanol desorption at 165 K, with spectra at 85 K and 130 K being displayed in Figure 6. Although not shown in the figure, no spectral variations were appreciated when heating the sample

Table 1
Assignment and Wavenumbers of CO₂-Dist Bands Recorded in This Work and Comparison with Previous Literature Data

Assignment	Co-Deposited (This Work)	Co-Deposited (Other Works)		Pure (This Work)	Pure (Other Works)		
	85 K	15 K ^a	10 K ^b	85 K	80 K ^c	80 K ^d	60 K ^e
ν_2	645	646	645	655	655	655	655
	654		657	661	660	660	660
ν_3 (¹³ C)	2275	2275	2275	2282	2282	2282	2283
ν_3	2339	2339	2340	2345		2343	2343
$\nu_1 + \nu_3$	3694	3697		3708	3708	3708	3708

Notes.

^a Bernstein et al. (2005).

^b Ehrenfreund (1999).

^c Hodyss et al. (2008).

^d Sandford & Allamandola (1990).

^e Gerakines et al. (1995): pure CO₂ at 15 K and warm-up to 60 K.

from 85 K to 105 K. It is important to recall here that most of the CO₂ was evaporated before this temperature in sequentially deposited samples (see Figure 5). However, in co-deposited mixtures, relevant spectral changes are only observed at 130 K, when the crystallization of methanol begins taking place.

At 130 K all CO₂ dist has evaporated from the ice matrix (gray trace in all panels of Figure 6). However, in the mixture richer in CO₂, part of the CO₂ norm remains trapped, as seen in the right-hand side panels. This fraction desorbs together with methanol at 150–170 K, as commented on in the discussion of the TPD experiments (see Section 3.1). From the TPD experiments it was shown that the amount of CO₂ co-desorbed with CH₃OH grows with increasing $p_{\text{CO}_2}/p_{\text{CH}_3\text{OH}}$ ratio (Figure 2). This is also in agreement with the spectral evidence in Figure 6. These results indicate that for high enough CO₂/CH₃OH ratios (~20% as will be discussed below) fairly large amounts of pure CO₂, responsible for the CO₂-norm absorption feature, can be occluded by crystalline CH₃OH formed from the amorphous phase at 130 K, and remain deposited on the substrate until 150–170 K.

3.3. Estimation of CO₂ Dist in CO₂/CH₃OH Ice Mixtures

Having ascertained the existence of two possible carbon dioxide structures, it is interesting to estimate the amount of CO₂ dist which can be accommodated in amorphous methanol samples. This value would help in the interpretation of spectra of astrophysical objects, providing a clue to the structure of the ices containing these two species, and to the temperature variations in their formation history. The IR absorption bands commented on in the previous sections can be used for this purpose.

The growth of the CO₂/CH₃OH molecular ratio with increasing partial pressure of CO₂, until the onset of the CO₂ norm, is illustrated in Figure 7, where a comparison is presented between sequential and co-deposited samples. Only CO₂ dist is formed for the pressure range indicated in the figure. For every p_{CO_2} value, the integrated absorbance of appropriate bands in the IR spectra allows one to determine $N_{\text{CO}_2}/N_{\text{CH}_3\text{OH}}$, the ratio of column densities of CO₂ and methanol, respectively, as described in Section 2. At a given value of p_{CO_2} , the CO₂-norm peak at 2343 cm⁻¹ starts developing. The corresponding pressure indicates the saturation pressure of CO₂ dist, $p_{\text{CO}_2}^0$. For the generation of co-deposited samples, the methanol vapor pressure was kept constant at 1.8×10^{-5} mbar, and different ice mixtures were grown by varying the CO₂ pressure, always at a constant temperature of 85 K. Under the conditions of the

Figure 7. The concentration of CO₂ dist in co-deposited (a) and sequentially deposited (b) mixtures of CO₂/CH₃OH expressed in column density ratio $N_{\text{CO}_2}/N_{\text{CH}_3\text{OH}}$ vs. partial pressure of CO₂. The vertical broken lines indicate the onset of the growing of the CO₂-norm structure. The experiments were carried out at 85 K. Two films of different thickness of amorphous methanol were grown for the sequential samples before admittance of CO₂. The thicker film admits more CO₂ molecules before saturation.

co-deposition experiments presented in Figure 7(a), the maximum CO₂-dist concentration is ~20%, and the onset of CO₂-norm formation appears at $p_{\text{CO}_2}^0 = 1.3 \times 10^{-5}$ mbar.

In the lower part of this figure (Figure 7(b)), two sets of sequentially deposited samples are illustrated, corresponding to methanol films of ~300 nm and ~550 nm, grown at a deposition rate of ~2.5 nm s⁻¹. In the sequential experiments, each methanol film is exposed to a CO₂ pressure for a few minutes, always again at a constant temperature of 85 K, until the intensity of the ν_3 IR band of CO₂ dist at 2339 cm⁻¹ stops

Figure 8. The concentration of CO₂ dist in co-deposited mixtures of CO₂/CH₃OH (the solid circles) and CO₂/H₂O (the open circles) expressed in column density ratio vs. partial pressure of CO₂. The experiments were carried out at 95 K. The vertical broken lines indicate the onset of the growing of the CO₂-norm structure. For water, this process occurs at much lower p_{CO_2} .

growing. The saturation pressure of CO₂ dist, $p_{\text{CO}_2}^0$, is reached at 1.2×10^{-6} mbar and 1.9×10^{-6} mbar for methanol films of thicknesses 300 and 550 nm, respectively. The maximum CO₂-dist concentration in sequential samples is $\sim 0.2\%$, i.e., two orders of magnitude less than in co-deposited samples. This result points out the low efficiency of the penetration of CO₂ into a methanol ice as compared to that of the trapping mechanism taking place in a simultaneous ice growing process. The CO₂ molecules must stay only at the surface or in the upper fraction of methanol ice in sequential samples.

As shown in Figure 7(b), the number of CO₂ molecules that adsorb on methanol depends on the thickness of the film deposited. The thicker methanol film admits a lower percentage of adsorbed CO₂ molecules. This behavior is in contrast with recent data from our group (Gálvez et al. 2008) for the adsorption of CO₂ on ASW, where the CO₂/H₂O molecular ratio was found to be independent of the layer thickness. It can be inferred that the structure of amorphous solid methanol is more compact than that of ASW and does not allow the diffusion of the CO₂ molecules deep into the solid layer.

To pursue the comparison between these two systems, we have plotted in Figure 8 the ratio N_{CO_2}/N_x , with $x = \text{H}_2\text{O}$ and CH₃OH for co-deposited samples formed at 95 K. The temperature of 85 K employed in most measurements of this work was chosen because of the very small sticking of CO₂ on amorphous CH₃OH at 95 K, but we have done this experiment at 95 K to allow comparison with the carbon dioxide/water system. The onset of CO₂ norm, and thus the segregation of a pure phase of CO₂, takes place at a much smaller value in ASW, indicating a lower miscibility of CO₂ with ASW than with amorphous solid methanol. This result, which parallels the higher solubility of CO₂ in liquid CH₃OH as compared with liquid water (see, for instance, Xia et al. 2004), is not surprising taking into account the relative strength of the various pairwise interactions between the three molecules considered.

The comparison of the CO₂/methanol data in co-deposited samples at 85 K (Figure 7(a)) and 95 K (Figure 8) reveals that the p_{CO_2} value for the onset of CO₂ norm is more than an order of magnitude smaller at the lower temperature, but the maximum CO₂-dist concentration is comparable for both temperatures (roughly 19% at 85 K compared with $\sim 15\%$ at 95 K).

Table 2
Desorption Energies for the CO₂/Methanol System

CO ₂ /Amorphous Methanol Ice T-ice (K)	p_{CO_2} (mbar)	E_d (kJ mol ⁻¹)
87	7.8×10^{-6}	20.0
89	2.3×10^{-5}	19.7
90	4.6×10^{-5}	19.4
CO ₂ /Crystalline Methanol Ice T-ice (K)	p_{CO_2} (mbar)	E_d (kJ mol ⁻¹)
89	7.8×10^{-6}	20.5
91	2.3×10^{-5}	20.1
93	4.6×10^{-5}	20.0

3.4. Specific Surface Area and Desorption Energies

In spite of the observed dependence of the adsorbed molecular ratio on the layer thickness, a rough estimate of the specific surface area (SSA) for adsorption of CO₂ on methanol ice can be evaluated from a fit of the experimental $N_{\text{CO}_2}/N_{\text{CH}_3\text{OH}}$ data to a Brunauer–Emmett–Teller (BET) isotherm (Brunauer et al. 1938; Rouquerol et al. 1999).

Following a procedure analogous to that described in Gálvez et al. (2008), a linear fit of the data in Figure 7(b), represented in a BET plot, was carried out in the range $0.01 < p_{\text{CO}_2}/p_{\text{CO}_2}^0 < 0.6$. The SSA can then be obtained by assuming an effective mean CO₂ molecular area of $15.5 \text{ \AA}^2$, a value already used in previous works (Sandford & Allamandola 1990, Gálvez et al. 2008), and consistent with the available crystallographic data (Simon & Peters 1980). With this assumption, we derived a value of SSA of $6.5 \pm 2 \text{ m}^2 \text{ g}^{-1}$ and $5.8 \pm 2 \text{ m}^2 \text{ g}^{-1}$ for the thin and thick methanol ice films of Figure 7(b), respectively. Note that for a film thickness variation close to a factor of 2, the values of the SSA derived for the two ice layers coincide within their estimated uncertainties, which gives an indication of the expected limiting value for this magnitude. The estimated SSA for the CO₂/CH₃OH system is appreciably smaller than that derived in a previous work for the CO₂/H₂O system using the same procedure ($39 \pm 15 \text{ m}^2 \text{ g}^{-1}$, Gálvez et al. 2008) and also smaller than the rest of the literature values for the SSA of CO₂ adsorbed on ASW (see Gálvez et al. 2008), which again suggests a much more compact, less porous structure in amorphous solid methanol than in ASW.

We have calculated the desorption energy of CO₂ from amorphous and crystalline CH₃OH surfaces following a procedure introduced by Sandford & Allamandola (1990) that we already used in our previous work on the interaction of CO₂ with water ice (Gálvez et al 2007). The method is based on the observation of the sticking of CO₂ over the ice as a function of CO₂ pressure and ice temperature. Amorphous and crystalline methanol ice layers were exposed to various CO₂ pressures and the amount of CO₂ deposited was monitored with the IR spectra. For each CO₂ pressure, the ice was cooled in 2 K steps from an initial temperature of 120 K until some evidence of CO₂ deposition was observed in the spectra. With the corresponding final temperature and using the effective mean CO₂ molecular area ($15.5 \text{ \AA}^2$ as mentioned above), and $\nu_0 = 2.9 \times 10^{12} \text{ s}^{-1}$ (frequency of oscillation of the adsorbed molecules on the surface) from Sandford & Allamandola (1990), we have determined the desorption energies listed in Table 2.

The average values obtained are $E_d = 19.7 \pm 2 \text{ kJ mol}^{-1}$ and $20.2 \pm 2 \text{ kJ mol}^{-1}$ for the adsorption of CO₂ on amorphous and crystalline methanol ices, respectively. The E_d for crystalline ice

is slightly higher, but the difference is small compared with the estimated uncertainties for these magnitudes, which are mostly due to the assumptions implied in the method. We are not aware of other experimental determinations of E_d for the $\text{CO}_2/\text{CH}_3\text{OH}$ system. The present values are very similar to those reported in our previous work (Gálvez et al. 2007) for $\text{CO}_2/\text{H}_2\text{O}$ ($20.7 \pm 2 \text{ kJ mol}^{-1}$ for ASW and $19.9 \pm 2 \text{ kJ mol}^{-1}$ for crystalline water ice) using the same experimental procedure, which indicates that the strength of the intermolecular interaction is comparable in both cases.

4. SUMMARY AND CONCLUSIONS

This work presents an investigation on ices formed by methanol and carbon dioxide—two of the main components found in solids in astrophysical media. In our laboratory, ices are grown on a liquid N_2 -cooled cryostat by simultaneous or sequential admission of the gases under controlled pressure and temperature conditions. The samples are analyzed using IR spectroscopy and mass spectrometry, which also allows TPD experiments to be performed.

In the range of temperatures spanned in this study, relevant for protostellar environments, comets, and solar system bodies, our investigation provides evidence, supported by both IR and TPD measurements, of two slightly different CO_2 structures, which can be referred to as “normal” and “distorted.” The vibrational modes of CO_2 norm appear at the same wavenumbers and with similar appearance as those of pure CO_2 crystals. This species is found on both kinds of deposition processes, sequential (first methanol and then carbon dioxide) or co-deposition, and can remain trapped inside crystalline methanol up to 150–170 K, the desorption temperature for this species, only when the ice is grown by simultaneous deposition. On the other hand, the vibrations of CO_2 dist are red-shifted between 5 and 10 cm^{-1} with respect to those of pure CO_2 . This distorted structure is released from the samples when heating above 130 K. Thus, the observation of vibrational bands with the characteristics described here for CO_2 dist in astrophysical media containing CO_2 and methanol mixtures implies a limit of 130 K on the temperature that the object has been subjected to.

The amount of CO_2 dist that can be retained in ices grown sequentially is about two orders of magnitude smaller than that which can be trapped if CO_2 were present during the growing process of the ice. The onset of the normal CO_2 structure in co-deposited samples, which indicates the saturation of the host ice and the segregation of pure CO_2 , takes place at a lower pressure in amorphous water ice than in methanol ice. This is understood as a smaller miscibility of CO_2 into ASW than into CH_3OH ice.

The response of simultaneously grown ices upon heating shows that for slow warming processes a higher amount of CO_2 can be retained in the ice during the methanol crystallization. Therefore, for very slow processes, such as those taking place in comet nuclei in their perihelion stage, the maximum amount of CO_2 will stay in the ice.

We have also determined the desorption energy E_d and specific surface area SSA for the system $\text{CO}_2/\text{methanol}$, from measurements of spectral absorbance values. The energy $E_d \sim 20 \text{ kJ mol}^{-1}$ turns out to be of comparable magnitude to that of the CO_2/water system which indicates that the adsorption processes on surfaces of amorphous water ice and solid methanol ice, either amorphous or crystalline, are of similar strength. On the other hand, the SSA value for methanol ice, $\sim 6 \text{ m}^2 \text{ g}^{-1}$, is much smaller than that of water ice, $\sim 39 \text{ m}^2 \text{ g}^{-1}$,

which can be interpreted in terms of the higher porosity of ASW than of methanol ice. CO_2 can penetrate easily into the pores and canals of ASW, but the structure of amorphous methanol ice must be more compact and allows only a limited access to the more external fraction of the ice. In astrophysical systems containing ASW and amorphous methanol ice, CO_2 molecules formed at a later stage would have a larger possibility to enter ASW than methanol ice. In contrast, if CO_2 is available during the growing process of the ice, methanol ice would admit a higher concentration of carbon dioxide than water ice. As for crystalline methanol ice, similarly to crystalline water ice, it does not allow any penetration at all of the molecules of carbon dioxide.

Although the present experiments have been carried out at temperatures greater than 80 K, the data on $\text{CO}_2/\text{CH}_3\text{OH}$ miscibility derived in this work can be of help for the analysis of observational results from protostellar environments, since once formed at low temperatures ($< 20 \text{ K}$) the ices of methanol and carbon dioxide are expected to remain stable until they evaporate in the range of temperatures contemplated in the present work (Aikawa et al. 2008). If CH_3OH and CO_2 are formed together in low-temperature reactions of CO with hydrogen and oxygen on grain surfaces, the amount of CO_2 embedded in CH_3OH could be relatively large, as suggested by the laboratory data on co-deposited samples. In this case, the actual proportion between the two components could even reflect the competition between simultaneous oxidation and hydrogenation reactions of CO on the cold grain surfaces. If, on the other hand, in a given environment the original ice is made mostly of CH_3OH (e.g., through prevalence of hydrogenation), the amount of CO_2 that could be incorporated later into the (amorphous) solid would be much smaller. The fact that a significant amount of CO_2 can remain trapped in the ice until crystallization of CH_3OH should be taken into account in the elaboration of gas-grain chemical models. The range of temperature studied in this work is also of interest for the modeling of cometary behavior (González et al. 2008) and, even when CH_3OH is not a major component of cometary ice, thermodynamic data on its interaction with CO_2 should be useful, for completeness, in the improvement of models on comets and other solar system bodies.

These results are expected to be relevant for the interpretation of observational data from, e.g., comet nuclei, near-Earth objects or asteroids, polar caps in planets and satellites of the solar system, and protostellar environments.

This research has been carried out with funding from the Spanish Ministry of Education, Project FIS2007-61686, and from the CSIC, Hielocris PIF2005. O.G. acknowledges financial support from the Ministry's “Juan de la Cierva” program. We are grateful to P. J. Gutiérrez (IAA, CSIC, Spain) and to an anonymous referee for helpful suggestions in the reviewing process.

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