

# A study of the interaction of CO<sub>2</sub> with water ice

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## ABSTRACT

**Aims.** We studied the interaction between CO<sub>2</sub> (guest) and H<sub>2</sub>O (host) molecular ices.

**Methods.** Ices of CO<sub>2</sub> and H<sub>2</sub>O are prepared by four different deposition techniques: sequential deposition (amorphous water ice followed by addition of CO<sub>2</sub>), co-deposition (both gases added simultaneously), inverse sequential deposition (carbon dioxide ice followed by addition of water) and crystalline sequential deposition (crystalline water ice is prepared first and CO<sub>2</sub> is added afterwards). Samples are deposited at 80 K and are studied by temperature programmed desorption and transmission infrared spectroscopy.

**Results.** Two slightly different varieties of association of CO<sub>2</sub> and H<sub>2</sub>O are revealed from the different spectroscopic properties of the asymmetric stretching band of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub>. The two varieties are found to co-exist in some of the samples at 80 K, whereas only the so-called internal CO<sub>2</sub> remains after heating at 105 K. At 80 K carbon dioxide is able to adhere to a crystalline water ice surface. Activation energies for the desorption of CO<sub>2</sub> from amorphous ( $E_d = 20.7 \pm 2$  kJ mol<sup>-1</sup>) and crystalline ( $E_d = 19.9 \pm 2$  kJ mol<sup>-1</sup>) water ice are derived from measurements of the sticking of CO<sub>2</sub> as a function of ice temperature.

**Conclusions.** These findings may have implications for the study of icy bodies of the Solar System.

**Key words.** molecular data – molecular processes – techniques: spectroscopic – methods: laboratory

## 1. Introduction

Ices, understood as condensed phases of e.g. H<sub>2</sub>O, CO, CO<sub>2</sub>, CH<sub>3</sub>OH, NH<sub>3</sub>, CH<sub>4</sub>, etc. are ubiquitous throughout the Universe. Ices can be found in dense and cold regions of the interstellar medium, where stars are initially born (Boogert & Ehrenfreund 2004; Ehrenfreund et al. 2003; Gerakines et al. 2005). In particular, the instruments on board the Infrared Space Observatory (ISO) revealed that H<sub>2</sub>O, CO<sub>2</sub> and CH<sub>3</sub>OH ices were even dominating grain surfaces in warm regions close to massive protostars (Dartois 2005; Van Dishoeck 2004; Ehrenfreund et al. 1997; and references therein). For Solar System research, ices are, in addition, of clear cosmogonic importance. Comets and Kuiper Belt objects are made up of dusty ices mixtures (see e.g. reviews by Crovisier 2006 and Meech & Svoren 2003). As they are, presumably, the less evolved objects of the Solar System, these bodies preserve information about the conditions under which our planetary system formed. At a closer view, ices are even vital for our own climate. Icy particles in our atmosphere significantly affect atmospheric chemistry (Hung et al. 2003; Baker 1997; Tolbert & Toon 2001).

Ices and ices mixtures have been studied from many different standpoints, with very different techniques. In the astrophysical context, part of the knowledge about their composition, physical state, microstructure, and evolution has been derived by means of spectroscopic studies, mainly in the infrared, comparing observational evidence with results from the laboratory. Some interesting investigations, to mention but a few, are: Bernstein et al. (2005, 2006), Gerakines et al. (2005), Grundy & Schmitt (1998), Moore & Hudson (1993), Moore et al. (2001), Quirico et al. (1996), Satorre et al. (2001), Schmitt et al. (1989), van Broekhuizen et al. (2006), etc. This kind of study has

provided the community with an important database on spectroscopic behavior of ices under very different conditions, which have allowed the detection of different ices in various astronomical environments. As an example, among many relevant ones, Sandford & Allamandola (1990) showed that laboratory spectra of CO<sub>2</sub> can be used both to derive column densities of CO<sub>2</sub> condensed in interstellar grains, and to obtain clues on the thermal history of interstellar ices. These results have been widely used as, for example, in the recent detection of CO<sub>2</sub> on Saturn's satellite Iapetus (Buratti et al. 2005).

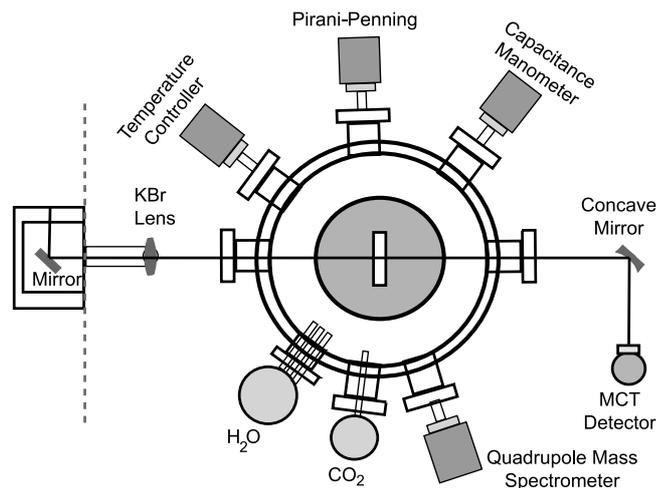
The ubiquity and importance of ices require steadfast efforts on a complete characterization of their behavior under different physical conditions. In the present investigation, we focus on mixtures of ices of H<sub>2</sub>O and CO<sub>2</sub>. A study in line with the present one was performed by Ehrenfreund et al. (1999). These authors studied infrared spectra of H<sub>2</sub>O, CO<sub>2</sub> and CH<sub>3</sub>OH ices mixtures, formed by co-deposition and exposed both to thermal and to UV irradiation processing. The main result from their study was that H<sub>2</sub>O, CO<sub>2</sub> and CH<sub>3</sub>OH bands can indeed be used to trace the evolution of ice composition in dense interstellar clouds. In the present investigation several deposition methods and different thermal histories will be studied. These various methods could represent different formation mechanisms and/or different evolutionary phases of icy mantles (e.g. Boogert & Ehrenfreund 2004). The evolution, as the temperature increases, of the various structures formed with the different deposition methods, and its implications both from thermophysical and spectroscopic standpoints, are of great importance not only to appropriately analyze and interpret remote spectroscopic data, but also for the modeling of the thermophysical evolution of Solar System minor bodies, among other possible applications.

Besides those already cited, there are a number of papers based on laboratory investigations on the field of the interaction between gases and water ice, using temperature-programmed desorption (TPD) techniques based on mass spectrometry (Viti et al. 2004; Notesco et al. 2003; Hudson & Donn 1991), molecular beam techniques (Andersson et al. 2004), or infrared spectroscopy (Bar-Nun & Laufer 2003), among many others. Two very recent papers deal with systems closely related to that of the present investigation, and will be discussed in greater detail. Collings et al. (2004) have carried out an extensive laboratory survey of astrophysical ices of several molecules, using TPD. They studied the adsorption of these molecules on a bare gold substrate, and also their adsorption on water films previously deposited (subsequently referred to in this article as sequential deposition), and after simultaneous deposition with water (co-deposition). They ranked the systems under study in three categories, according to their volatility or similarity to water. Thus, CO, N<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub> are the most volatile; NH<sub>3</sub>, CH<sub>3</sub>OH and HCOOH are the least volatile or closest to water; and H<sub>2</sub>S, OCS, C<sub>2</sub>H<sub>2</sub>, SO<sub>2</sub>, CH<sub>3</sub>CN, and CO<sub>2</sub> are intermediate species. The molecule studied in this work, carbon dioxide, falls therefore into the third type. The findings of Collings et al. are discussed below, in comparison with our present results. On the other hand, Kumi et al. (2006) have presented a thorough study on the guest-host interactions of amorphous solid water (ASW) with CO<sub>2</sub> and N<sub>2</sub>O molecules, using Fourier transform infrared spectroscopy (FTIR). Based on spectra taken at their deposition temperature (90 K) and after heating to higher temperatures, they were able to propose a mechanism for the adsorption, binding and transport of these two molecules in ASW films. Again, the results of the present investigation will be compared to those of Kumi et al. in the appropriate sections below.

Our research uses a combination of the two techniques mentioned above, TPD and FTIR, on a variety of experimental conditions. We have studied water/CO<sub>2</sub> systems in an approximate 15/1 ratio. The samples were prepared by four deposition techniques. The behavior of the samples on heating is also investigated. The objective of this research is to throw some more light on the adsorption and diffusion processes that take place between the guest (CO<sub>2</sub>) and host (H<sub>2</sub>O) molecular ices. We find it particularly interesting that some of our results reproduce closely those of the above mentioned references, but others show different characteristics. Besides, we present new evidence, notably on spectra of co-deposited samples. We have also measured activation energies for the desorption of CO<sub>2</sub> from amorphous and crystalline water ice from spectroscopic experiments.

## 2. Experimental part

Our experimental set-up shown in Fig. 1 has been described in detail before (Carrasco et al. 2002; Escribano et al. 2003; Maté et al. 2003; Maté et al. 2006). In brief, it consists of a high vacuum cylindrical chamber, evacuated by a turbomolecular pump, in whose interior a sample holder, connected to a liquid nitrogen Dewar, provides the appropriate substrate for the deposition of the systems to be studied. The chamber pressure is monitored between 1000 and 10<sup>-9</sup> mbar by a combination of a pirani and a penning gauge. In addition, a capacitance manometer (Leybold, Ceravac CTR81) provides absolute pressure readings in the 10<sup>-2</sup>–10<sup>-5</sup> mbar range. The background pressure in the chamber is usually smaller than 10<sup>-8</sup> mbar. The chamber is coupled to a Fourier transform infrared spectrometer Bruker IFS66 through a purged pathway, with KBr windows for the incident and transmitted radiation, which is focused on exit onto a



**Fig. 1.** Scheme of the experimental set-up used for the deposition and study of the ice films.

liquid-N<sub>2</sub> refrigerated MCT detector. In the transmission set-up used in the present experiments, the substrate on which samples are deposited is a Si wafer of about 1 mm thickness. The IR spectrum of this wafer is used as background for ratioing the spectra of the different samples. Spectra are recorded with a nominal resolution of 2 cm<sup>-1</sup> (corresponding to ~0.5 cm mirror displacement), with 512 co-added scans for each spectrum. A three term Blackman-Harris apodization function is used in all cases. The substrate is mounted on a holder that allows temperature control, with about 1 K accuracy, between 80 and 220 K. Heating is performed using a power transistor (2N3055). Controlled flows of CO<sub>2</sub> and water vapor are introduced into the chamber through needle valves. The chamber has inlets for the insertion of gases, and is coupled by means of a regulation valve to a differentially pumped chamber containing an Inficon, Transpector 2 quadrupole mass spectrometer (QMS), which is used to monitor the vapor composition during the deposition and heating processes. A pressure difference of two orders of magnitude was usually maintained between the deposition and the quadrupole chamber. Typical deposition pressures are always below 10<sup>-4</sup> mbar.

Films of H<sub>2</sub>O/CO<sub>2</sub> ice were prepared in different ways (see below) by vapor deposition on the substrate held at a temperature of ~80 K. Distilled water and 99.998 % purity CO<sub>2</sub> from Air Liquide were used in all experiments. To monitor the thickness and H<sub>2</sub>O/CO<sub>2</sub> ratio in each experiment, combined use of spectral data and quadrupole measurements was made, according to the following scheme. For pure water, the film thickness can be easily controlled through the interferences of a normal-incident He-Ne laser (Maté et al. 2003), and for a given thickness value, comparison to literature absorbance data (Léger et al. 1983) allows the estimation of the amount of water deposited on the substrate. Similarly, the observed absorbance of a given sample of pure CO<sub>2</sub>, compared to previous measurements (Ehrenfreund et al. 1997), can be used to calibrate the QMS with sufficient accuracy. Then, for any kind of deposition scheme, the quadrupole readings can be used to select the amount of either gas introduced into the chamber. An H<sub>2</sub>O:CO<sub>2</sub> value of ~15:1 was chosen for the present investigation. Typical thickness values of 0.3 μm were estimated for the water ice films at each side of the substrate. A sticking efficiency of 1.0 was assumed for both species at 80 K, although in the case of pure CO<sub>2</sub> this value could be slightly lower (Sandford & Allamandola 1990).

The four different deposition procedures employed for the generation of the various types of samples are the following:

- *Sequential deposition*: first the host species, water, is deposited at 80 K as amorphous (ASW), and then CO<sub>2</sub> is added at the same temperature, until the chosen ratio host/guest, is accomplished.
- *Co-deposition*: water and CO<sub>2</sub>, are introduced into the chamber simultaneously, at the appropriate ratio, and deposited on the substrate at 80 K.
- *Inverse sequential deposition*: first the desired amount of CO<sub>2</sub> is introduced into the chamber with the substrate at 80 K. At this temperature, crystalline CO<sub>2</sub> is expected to form. Water is then admitted, always keeping the substrate at the same temperature, until the chosen guest/host ratio is reached.
- *Crystalline sequential deposition*: water is first deposited at 80 K. The temperature is then raised up to 165 K and kept there for five minutes to induce crystallization from the amorphous phase. The crystalline water film is subsequently cooled to 80 K, and CO<sub>2</sub> is then admitted until the desired ratio is achieved.

Both TPD and IR absorption measurements were performed on the various ice films. The TPD measurements covered the range 80–190 K, which includes the desorption peaks corresponding to the stronger guest-host interactions. Most of the weakly bound CO<sub>2</sub> was desorbed at nominal temperatures around 90–110 K, but in this temperature interval part of the desorbed CO<sub>2</sub> comes from cold cryostate surfaces apart from the substrate. It is difficult to estimate the contribution of this kind of desorption, which gives rise to an artificial broadening of the peaks, and we have not considered these results here. No more CO<sub>2</sub> is seen to desorb until a temperature above 150 K, and therefore our study deals with the 150–190 K range. A heating ramp of 0.3 K s<sup>-1</sup> was used for the TPD experiments. Due to some difficulties for the synchronization of the QMS with the heating ramp, there is an uncertainty of approximately 5 K in the absolute temperature scale of the TPD graphs.

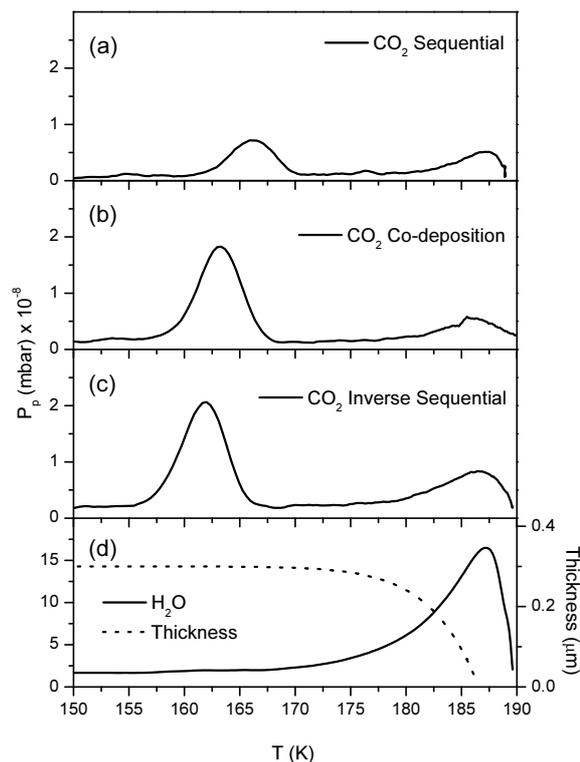
Infrared spectra of the four types of film described above were recorded at 80 K, the lowest film temperature, and at 105 K, where some modifications in the CO<sub>2</sub> spectra were observed. These changes are more clearly seen in the CO<sub>2</sub> asymmetric stretch  $\nu_3$  band, shown in detail below. Spectra recorded between 105 K and the temperature of H<sub>2</sub>O crystallization, ~165 K, did not show significant variations.

Additional measurements were performed on CO<sub>2</sub> sequentially deposited, both on amorphous and crystalline water ice. FTIR spectra were recorded as a function of the ice temperature for various CO<sub>2</sub> pressures, starting from 120 K and cooling until the first evidence of CO<sub>2</sub> was found in the spectra. The corresponding data were used for the estimation of desorption activation energies.

### 3. Results and discussion

#### 3.1. TPD experiments

Figure 2 contains the most relevant results for our desorption experiments between 150 and 190 K. Due to the synchronization problems mentioned above, the abscissa values have to be taken with an uncertainty of ~5 K. The three upper panels correspond to the desorption of CO<sub>2</sub> from CO<sub>2</sub>/amorphous water samples and the lowest one to the desorption of the host water layer. Water desorption, with a maximum at about 185–190 K,



**Fig. 2.** TPD graphs for CO<sub>2</sub>/H<sub>2</sub>O ices deposited as specified (see text). The ordinate scale indicates QMS readings. *From top to bottom*: CO<sub>2</sub> curves for sequential deposition, co-deposition and inverse sequential deposition, and H<sub>2</sub>O curve, plus estimation of sample thickness using Eqs. (1) and (2).

is similar in all cases and only one trace is shown for simplicity. A theoretical estimate of the desorption of the water film, based on a simple model, is also presented in the lowest panel (see below). In the case of CO<sub>2</sub>/crystalline water all the CO<sub>2</sub> was desorbed at  $T < 130$  K, and consequently it is not included in the figure. The signals corresponding to co-deposition and inverse sequential deposition are similar. Both show two maxima, one close to 165 K and a smaller one at about 185 K, coincident with the water peak. The location and intensity of the first desorption maximum are alike, the second maximum being somewhat larger in the inverse deposition experiment. Also two maxima at the same temperatures, within experimental uncertainty, albeit of lower intensity, are observed in the sequential deposition sample.

Several authors have studied the release of CO<sub>2</sub> and other gases from water ice (e.g. Bar-Nun et al. 1985; Hudson & Donn 1991; Collings et al. 2004). Although all of these investigations coincide with the observation of two desorption peaks for CO<sub>2</sub> in this temperature range, the actual temperature values measured for these peaks vary from one study to another, and furthermore the water maximum is found at different temperatures. The desorption of the water layer can be approximately modeled. Assuming zero-order kinetics, the time derivative of the film thickness as a function of temperature can be expressed as (Maté et al. 2003):

$$\frac{dx}{dt} = -\frac{a_0}{\rho} \exp\left(-\frac{E_d}{RT}\right) \quad (1)$$

where  $x$  is the film thickness,  $\rho$  is the water density in the deposited film,  $E_d$  the desorption activation energy,  $a_0$  the pre-exponential factor for zero-order kinetics,  $T$  the

surface temperature and  $R$  the gas constant. Equation (1) can be integrated over a given temperature interval by introducing the heating rate,  $v_h = (dT/dt)$ .

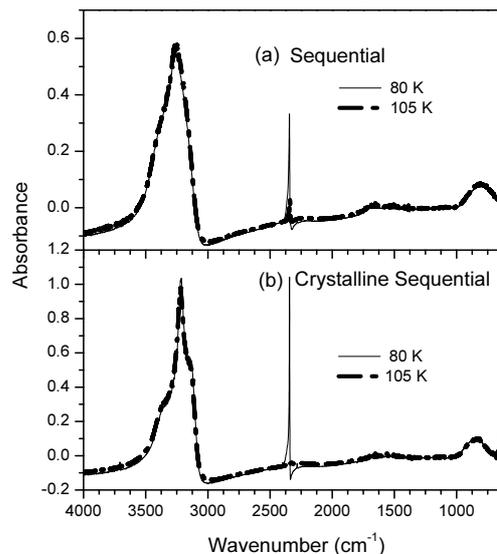
$$\int_{x_i}^{x_f} dx = - \int_{T_i}^{T_f} \frac{a_0}{v_h \rho} \exp\left(-\frac{E_d}{RT}\right) dT \quad (2)$$

where  $x_i$  and  $x_f$  are the initial and final thickness of the layer, and  $T_i$  and  $T_f$  the corresponding temperatures. Using Eq. (2) we have calculated the evolution of the water film thickness during our TPD experiments, with the result represented as a dotted line in the lower panel of Fig. 2. As can be seen, the calculated desorption corresponds well with the location of the measured TPD peak. The pre-exponential factor and the values of the desorption energy and water density used for the integration of Eq. (2) were:  $a_0 = 2.8 \times 10^{30}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ ;  $E_d = 49.8$  kJ  $\text{mol}^{-1}$  and  $\rho = 2.74 \times 10^{22}$  molecules  $\text{cm}^{-3}$ . These values were taken from Haynes et al. (1992) and Brown et al. (1996), and had already been used for estimates of water film thickness in a previous study by our group (Maté et al. 2003). As indicated above, the heating rate of our present experiments was  $v_h = 0.3$  K  $\text{s}^{-1}$ . Given the uncertainty in the parameters of the model (Haynes et al. 1992; Brown et al. 1996) and the imprecision in the absolute temperature scale mentioned above, the good agreement between model and measurements could be a bit fortuitous, but in any case, the essential picture provided by Eqs. (1) and (2) seems to be correct.

The desorption of crystalline water films should take place at a slightly higher temperature, given the higher desorption energy of crystalline films reported in the literature (Sandford & Allamandola 1990; Sack & Baragiola 1993). However, the difference is small and is expected to lie within the experimental uncertainty of the present measurements. Similar observed temperature values and good agreement with the predictions of Eqs. (1) and (2) for the water desorption peak are reported by Bar-Nun et al. (1985) (observed maxima at  $\sim 180$ – $200$  K and predictions at 180–190 K), and Hudson & Donn (1991) (observed at  $\sim 175$  K, predicted at 179 K). However, this value is measured at  $\sim 160$  K by Collings et al. (2004), whereas the application of the simple model would yield a value of 179 K for the reported experimental conditions of that work. The reason for this discrepancy is not obvious. A density of  $\rho \sim 2 \times 10^{22}$  molecules  $\text{cm}^{-3}$  was assumed in the model calculations for these experiments. This value should correspond (Brown et al. 1996) approximately to the conditions of Bar-Nun et al. (1985) and Hudson & Donn (1991), who deposited their samples at 20–30 K. The depositions of Collings et al. (2004) were performed at 10 K and for this temperature no values of  $\rho$  were reported (Brown et al. 1996). However, an appreciable change in density between 10 and 20 K would be needed to reconcile predictions and measurements.

Collings et al. also measured two CO<sub>2</sub> desorption peaks in this range. Our values are again shifted by about 20 K to higher temperatures, agreeing nonetheless with these authors in their separation and relative position to the water maximum.

The explanation given by Collings et al. (2004) for the two peak structures can be also applied to our experiments. The peak at  $\sim 165$  K would thus correspond to the “volcano” desorption and the smaller peak at about 185 K is due to the co-desorption of the last trapped CO<sub>2</sub> molecules together with the water ice. The abrupt volcano desorption described by Smith et al. (1997) takes place through connected pathways formed in the water layer during the nucleation and growth of crystalline ice from ASW. The fact that our CO<sub>2</sub> volcano desorption peak is shifted by  $\sim 20$  K toward temperatures higher than that of

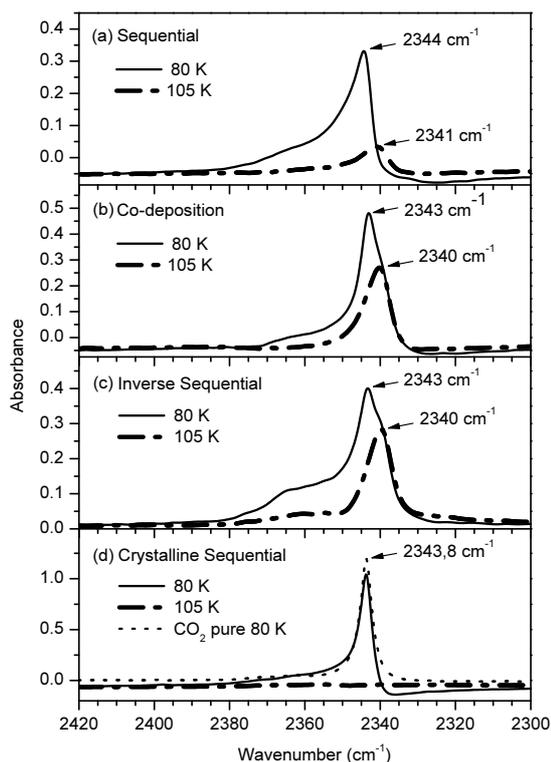


**Fig. 3.** IR spectra of H<sub>2</sub>O and CO<sub>2</sub> mixtures in **a)** sequential and **b)** crystalline sequential deposition experiments, in the full mid-IR range recorded.

Collings et al. (2004) – precisely the same shift found between the peaks for the desorption of water – suggests that most of the water layer must crystallize before a significant amount of the trapped CO<sub>2</sub> is released. The crystallization rate of the water layer is determined by its thickness, density and heating rate. In accordance with the measurements of Collings et al., the volcano desorption peak in our experiments is stronger than that of co-desorption. The implications of this result for the interaction between the CO<sub>2</sub> and the ASW host layer are not yet clear. A comparison of the peak heights in the TPD records of the three different H<sub>2</sub>O/CO<sub>2</sub> samples is also illustrative. The weaker desorption peaks found for the sequential deposition case show that a smaller amount of CO<sub>2</sub> is incorporated into the bulk water sample, as expected. Interestingly, no significant differences are observed between the desorption peaks of co-deposited samples and samples from inverse sequential deposition. For the samples of CO<sub>2</sub> deposited on crystalline water mentioned above, the absence of CO<sub>2</sub> desorption peaks for  $T > 130$  K indicates that no CO<sub>2</sub> is incorporated into the crystalline water ice. A more detailed study of the desorption kinetics of CO<sub>2</sub> from water ice would be needed for full interpretation of these results.

### 3.2. FTIR spectra

Figure 3 presents IR spectra of sequentially deposited samples, initially at 80 K and after heating at 105 K. The upper frame shows the spectrum corresponding to sequential deposition and the lower panel to that of the crystalline sequential experiment. The water to CO<sub>2</sub> ratio is  $\sim 15$ :1, as in all the experiments described in this work. This figure is shown to highlight the following effects. The change between amorphous and crystalline water is reflected by the well-known narrowing of the O-H stretching region, 3000–3500  $\text{cm}^{-1}$ , whereas the rest of the spectrum is practically unaffected. The consequence of the narrowing of the band is also an increase in the maximum absorbance of the peak (note the different absorbance scale in the two frames), keeping the overall band intensity unchanged. Interestingly, similar effects are observed on the  $\nu_3$  band of CO<sub>2</sub>, which also becomes narrower (not easily seen in this compressed figure; see below where expanded traces of the spectra are shown



**Fig. 4.** IR spectra of samples of sequential deposition, co-deposition, inverse sequential deposition and crystalline sequential deposition, **a)** to **d)**, respectively. All spectra at  $2\text{ cm}^{-1}$  resolution, and at temperatures indicated in each graph.

and discussed) and with a higher peak absorbance. Although at the deposition temperature of our experiments (80 K) CO<sub>2</sub> is expected to build up a crystalline solid, the fact that the substrate is crystalline rather than amorphous water induces an apparently higher degree of crystallinity in the CO<sub>2</sub> structure (Albella 2003). Finally, the dashed trace of the 105 K spectrum in the lower frame indicates that all CO<sub>2</sub> has been desorbed at this temperature.

As mentioned above, the expanded region of the  $\nu_3$  band of CO<sub>2</sub> allows a better observation of spectral changes induced by the heating of the samples, as no significant variations are detected in the spectra of water in this spectral zone. Figure 4 shows transmission IR spectra of the mixtures of water and CO<sub>2</sub> in this region. The samples were deposited at 80 K, and spectra were recorded at this temperature. They were then heated and kept at 105 K until no variation was detected in the quadrupole spectrometer, indicating that gas release at this temperature was completed. This happened systematically in less than 2 minutes. Spectra were subsequently registered. Note that the intensity scale takes fairly large values in absorbance units, which indicates that strong absorptions of CO<sub>2</sub> are taking place in all samples. The top panel corresponds to sequential deposition; it can be seen that after heating, a weaker band appears at  $\sim 2341\text{ cm}^{-1}$ , i.e. shifted by  $\sim 3\text{ cm}^{-1}$  to lower wavenumber. The next panel represents a co-deposited sample. The spectrum at 80 K shows a maximum at  $2343\text{ cm}^{-1}$ , with a shoulder on the low-frequency slope of the main band; after heating, this shoulder is revealed as a clear band peaking at  $\sim 2340\text{ cm}^{-1}$ . Panel (c) displays the spectra corresponding to the inverse sequential deposition experiment, and presents a very similar pattern to that of co-deposited samples, although in this case an ASW layer has grown on top

of CO<sub>2</sub> ice. Finally, the bottom panel shows the spectra of CO<sub>2</sub> sequentially deposited on crystalline water. After heating, all CO<sub>2</sub> is desorbed from the sample. The spectrum of pure CO<sub>2</sub> is also displayed for comparison. The main difference between the spectrum of pure CO<sub>2</sub> and that deposited at 80 K on crystalline water is the asymmetry of the  $\nu_3$  band of the latter, which is also a feature of the 80 K spectrum of the sequential sample. The global consideration of the previous results indicates that there are two different mechanisms of interaction of CO<sub>2</sub> and water, leading to two slightly different CO<sub>2</sub> structures. The most relevant one at 80 K is characterized by a strong peak at  $\sim 2343\text{--}2344\text{ cm}^{-1}$ , close to that of pure CO<sub>2</sub>. In the second CO<sub>2</sub> structure the main peak is shifted to a lower frequency, at  $\sim 2340\text{ cm}^{-1}$ . This shifting must be due to the interaction of CO<sub>2</sub> with surrounding water, resulting in a slight weakening of the C-O bond, the lower frequency indicating a reduced value of the effective stretching force constant. Thus, to avoid lexical repetitions we may term these two structures CO<sub>2</sub>-ext and CO<sub>2</sub>-int, for external and internal, respectively, meaning by external that the interaction with water is quite weak as it would be if CO<sub>2</sub> were superficially adsorbed, for instance, and by internal the situation taking place when CO<sub>2</sub> molecules enter the pores of ASW. These two possible mechanisms have been discussed by Kumi et al. (2006), and we will emphasize here only those aspects that supply new evidence for this problem.

When CO<sub>2</sub> is sequentially deposited at 80 K (panel a of Fig. 4), it forms a structure with very little interaction with the host surface, as indicated by the position of the  $\nu_3$  band, and apparently without entering the amorphous water structure, given the absence of any low-frequency shoulder on that band. This CO<sub>2</sub> layer can be very thick, giving a strong infrared absorption signal. After heating, the CO<sub>2</sub>-ext is fully desorbed, but a small fraction is kept inside the ASW, as shown by the weak spectral absorption peak at  $\sim 2340\text{ cm}^{-1}$  at 105 K.

In co-deposition experiments, panel b, the two CO<sub>2</sub> structures coexist at 80 K. The main band has a peak at the frequency of the CO<sub>2</sub>-ext structure and a small shoulder at that of the CO<sub>2</sub>-int form. When the sample is heated, one band only at the CO<sub>2</sub>-int frequency remains, stronger than the corresponding shoulder observed at 80 K. This therefore indicates, on one hand, that no CO<sub>2</sub>-ext is kept, and on the other that apparently a fraction penetrates the bulk amorphous water, or adopts the CO<sub>2</sub>-int structure.

Panel c in Fig. 4 shows the spectra recorded after inverse sequential deposition. The pattern is similar to that of co-deposition, with the strongest peak at 80 K corresponding to CO<sub>2</sub>-ext, and a shoulder at the vibrational frequency of the CO<sub>2</sub>-int structure. After heating, only CO<sub>2</sub>-int remains. When water is deposited on top of a CO<sub>2</sub> ice, part of the CO<sub>2</sub> breaks its own crystalline structure and diffuses into the amorphous water layer above. The pressure that the ASW layer exerts on the CO<sub>2</sub> ice could be high enough to enable this effect, which is not observed when CO<sub>2</sub> is deposited on top of ASW in direct sequential deposition experiments. Kumi et al. (2006) performed a series of measurements in which CO<sub>2</sub> is “sandwiched” between two amorphous water films, and their results also prove that the pressure of the ASW layer on top of the CO<sub>2</sub> structure increases the formation of CO<sub>2</sub>-int.

Since the spectra recorded at 140 K (not shown here) do not present any significant variations with respect to those taken at 105 K, we may conclude that in all cases, the CO<sub>2</sub> diffused in the interior of ASW remains included until the water crystallization takes place, at  $\sim 165\text{ K}$ .

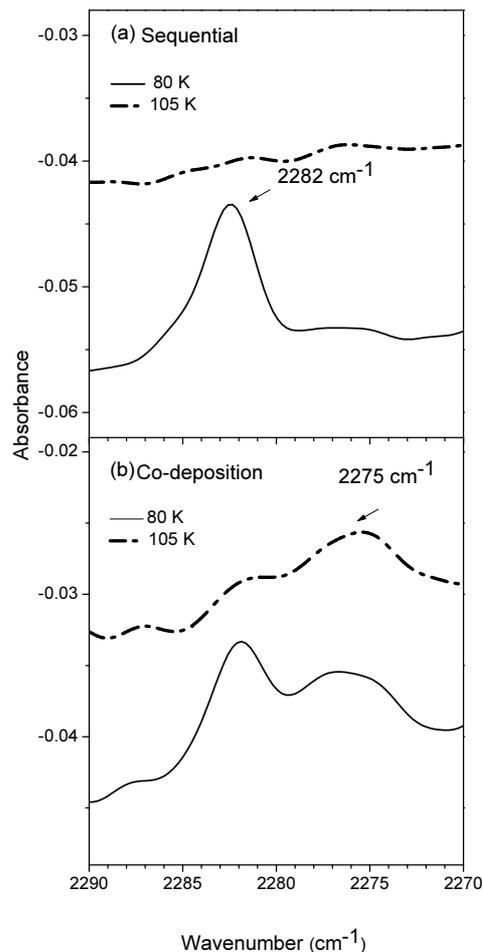
Panel d of Fig. 4 displays the spectra corresponding to CO<sub>2</sub> deposition on crystalline water. At 80 K the CO<sub>2</sub> is retained

on the surface but, as indicated in the previous comments on the TPD measurements, this layer of CO<sub>2</sub> desorbs completely upon heating and is unable to penetrate the crystalline ice structure. Kumi et al. describe this situation in terms of closing of the pores existing in amorphous water during the crystallization. Comparison of panels a and d reveals the different CO<sub>2</sub> adsorption mechanism at 80 K for ASW and for crystalline water, as a consequence of the different nature of the corresponding water surfaces. The contour of the CO<sub>2</sub>  $\nu_3$  band is sharper in the crystalline water experiment, and is in fact closer to that of a pure CO<sub>2</sub> sample grown directly on the substrate, shown also in panel d. It can be inferred from this that CO<sub>2</sub> adopts a more homogeneous structure when grown on top of a crystalline surface. It is also worth observing that the bandshape of the spectra of CO<sub>2</sub> adsorbed both on the amorphous and crystalline water surfaces is clearly asymmetrical, with an intensity drop on the low-frequency side, whereas in the spectrum of pure CO<sub>2</sub> ice this band is more symmetrical. This effect could be interpreted in terms of the interaction of CO<sub>2</sub> with the surface of water, which induces a modified structure for the first CO<sub>2</sub> layer in contact with the water surface (Ovchinnikov & Wight 1993).

The P-polarized transmission spectra presented by Kumi et al. were obtained at low exposure pressure, namely  $4 \times 10^{-8}$  Torr for CO<sub>2</sub>, and the films formed under these conditions are more favorable for the observation of weak effects, such as the appearance of a thin peak at  $2379 \text{ cm}^{-1}$  in a sequential deposition experiment at 90 K. This peak is present as a weak and broader feature shifted to  $\sim 2370 \text{ cm}^{-1}$  in all our spectra at 80 K, and has been interpreted as the longitudinal mode coupled to the transverse mode at  $\sim 2343 \text{ cm}^{-1}$  (Ovchinnikov & Wight 1993). Kumi et al. recorded spectra of the very weak amount of CO<sub>2</sub> that remains embedded into their thin ASW films upon heating at 105 K, which we have called here CO<sub>2</sub>-int. The peak absorption of the corresponding  $\nu_3$  band reaches a maximum of  $\sim 0.02$  for a water film of  $\sim 65$  layers, becoming saturated, and not increasing at higher doses of CO<sub>2</sub> at 90 K. This weak peak is also observed in our sequential deposition spectrum at 105 K, corresponding to experiments similar to those of Kumi et al., but performed on thicker water layers. In contrast, our results for co-deposition and inverse sequential deposition allow a much stronger absorption to be recorded for the  $\nu_3$  band of the CO<sub>2</sub>-int structure, with a peak absorbance of  $\sim 0.25$  in panels b and c. This proves that for higher water/CO<sub>2</sub> ratios in the co-deposition or in the inverse sequential deposition scheme, the intensity of that peak is increased, indicating a larger amount of CO<sub>2</sub> introduced within ASW, in agreement with the conclusions of Kumi et al., that the higher water to CO<sub>2</sub> ratio allows more CO<sub>2</sub> to occupy sites or vacancies inside the ASW structure.

The region corresponding to the same band for <sup>13</sup>CO<sub>2</sub> provides clearer evidence of the co-existence of the two CO<sub>2</sub> structures, as the shift between them is larger for this isotope. Figure 5 presents zoomed-in spectra in the  $\nu_3$  region of <sup>13</sup>CO<sub>2</sub>,  $\sim 2280 \text{ cm}^{-1}$ , recorded for sequential deposition (top) and co-deposition (bottom). At 80 K (solid line), only one peak is seen in the first case, corresponding to <sup>13</sup>CO<sub>2</sub>-ext, and two peaks in the second, arising from both <sup>13</sup>CO<sub>2</sub>-ext and <sup>13</sup>CO<sub>2</sub>-int, with a displacement of  $\sim 7 \text{ cm}^{-1}$ . At 105 K the CO<sub>2</sub>-ext trace has almost completely vanished, and the CO<sub>2</sub>-int spectrum is detected by a very weak peak in the co-deposition experiment only (dotted-dashed line).

We can make use of a simple molecular model based on Wilson's GF matrix scheme (Wilson et al. 1955) to gain insight into the properties of the  $\nu_3$  asymmetric stretching mode. Both the G and F matrices are one-dimensional for this vibration, with



**Fig. 5.** IR spectra of the  $\nu_3$  band of <sup>13</sup>CO<sub>2</sub> for **a)** sequential and **b)** co-deposited samples, at the temperatures indicated.

matrix elements  $g = 2\mu_C + \mu_O$  and  $f = f_{st} - f'_{st-st}$  respectively. The  $\mu_x$  are the reciprocal masses of the corresponding atoms ( $x = O$  or  $C$ ), and  $f_{st}$  and  $f'_{st-st}$  represent the force constants for the stretching of the C-O bond and for the interaction between both stretchings, respectively. The frequency of the  $\nu_3$  mode is therefore given by the following equation (Herzberg 1991):

$$\nu = \frac{1}{2\pi c} \sqrt{(f_{st} - f'_{st-st})(2\mu_C + \mu_O)}. \quad (3)$$

A frequency shift of  $\sim 4 \text{ cm}^{-1}$  in the wavenumber of this vibration, from  $\sim 2344$  to  $\sim 2340 \text{ cm}^{-1}$ , would therefore correspond to a weakening of the  $f_{st}$  force constant of the <sup>12</sup>CO<sub>2</sub>-int structure with respect to that of <sup>12</sup>CO<sub>2</sub>-ext by a factor of  $f_{st}^{int}/f_{st}^{ext} \sim 0.997$ , or 0.3%. The effect of the surrounding water molecules on the CO<sub>2</sub>-int structure can be estimated to be of that magnitude. Note also that in this simple model the C-O bond length is not relevant. For the <sup>13</sup>C vibration, where the shift is larger,  $\sim 7 \text{ cm}^{-1}$  from  $\sim 2282$  to  $\sim 2275 \text{ cm}^{-1}$ , the weakening effect is also slightly more marked,  $f_{st}^{int}/f_{st}^{ext} \sim 0.994$ . This is due to the fact that the <sup>13</sup>CO<sub>2</sub>-ext vibration does not strictly follow the isotopic mass ratio expected from Eq. (3) (predicted at  $\sim 2277 \text{ cm}^{-1}$  and observed at  $\sim 2282 \text{ cm}^{-1}$ ), whereas the vibration of the <sup>13</sup>CO<sub>2</sub>-int structure complies more closely with it (predicted at  $\sim 2273 \text{ cm}^{-1}$ , observed at  $\sim 2275 \text{ cm}^{-1}$ ).

In a very recent investigation, Chaban et al (2007) calculated the harmonic and anharmonic vibrational frequencies of clusters of CO<sub>2</sub> and a number of water molecules by ab initio methods.

**Table 1.** Ice temperatures for which CO<sub>2</sub> adsorption ceases as a function of CO<sub>2</sub> pressure.

CO <sub>2</sub> -amorphous water ice		
<i>T</i> -ice (K)	<i>P</i> -CO <sub>2</sub> (mbar)	<i>E<sub>d</sub></i> (kJ mol <sup>-1</sup> )
90	7.0e-6	20.8
92	1.4e-5	20.7
98	1.0e-4	20.5
CO <sub>2</sub> -crystalline water ice		
<i>T</i> -ice (K)	<i>P</i> -CO <sub>2</sub> (mbar)	<i>E<sub>d</sub></i> (kJ mol <sup>-1</sup> )
90	2.3e-5	19.9
93	4.8e-5	20.0
95	1.0e-4	19.8

They found a shift towards higher frequencies when one or two water molecules are added to pure CO<sub>2</sub>, in agreement with some observations on planetary satellites. The structure of the clusters studied by Chaban et al (2007) is probably very different to that of the ice systems investigated in this paper, and thus our respective results cannot be directly compared.

### 3.3. Desorption energies

Energies of desorption are often derived from TPD measurements. However, this procedure is problematic in the present case. In addition to the already mentioned experimental difficulties for the observation of neat desorption peaks below ~110 K with the available cryostat (Sect. 2), the CO<sub>2</sub> desorption energies from CO<sub>2</sub> surfaces and from H<sub>2</sub>O surfaces are similar (Sandford & Allamandola 1990). Thus, even if it were possible to measure the CO<sub>2</sub>-H<sub>2</sub>O (monolayer) desorption it would be very difficult to distinguish it from the CO<sub>2</sub>-CO<sub>2</sub> desorption. Therefore, rather than using TPD measurements we have employed a method analogous to that of Sandford and Allamandola (1990) based on the observation of the sticking of CO<sub>2</sub> to the ice surfaces as a function of CO<sub>2</sub> pressure and ice temperature. In our experiments sequential deposition was performed on the surfaces of pure amorphous and crystalline water ice and the amount of deposited CO<sub>2</sub> was monitored with FTIR measurements. For a given CO<sub>2</sub> pressure, the initial ice temperature was cooled from 120 K down in 2 K intervals until some evidence of CO<sub>2</sub> deposition was observed in the FTIR spectra. The results of these measurements, which were found to be very repetitive, are listed in Table 1 together with the desorption energies obtained from them.

For the derivation of the  $E_d$  values it was assumed that CO<sub>2</sub> deposition ceases when the average residence time of the molecules on the surface,  $t_s$ , is equal to the time during which the ice surface is hit by a number of CO<sub>2</sub> molecules equivalent to one monolayer coverage,  $t_m$ . It was further assumed that the desorption of CO<sub>2</sub> from ice surfaces can be described by the models of Langmuir (1916) and Frenkel (1924) in which  $t_s$  is given by

$$t_s = t_0 \exp(E_d/RT) \quad (4)$$

where  $E_d$  is the activation energy for desorption and  $t_0$  the period of oscillation of the molecule at the surface. The value of  $t_m$  was obtained as

$$t_m = \frac{n_s}{\varphi} \quad (5)$$

where  $n_s$  is the CO<sub>2</sub> monolayer surface density and  $\varphi$  is the flow of molecules to the surface for a given CO<sub>2</sub> pressure. For

the estimation of  $n_s$ , a mean seat area of 15.5 Å<sup>2</sup> (Sandford & Allamandola 1990; Barret & Meyer 1965) was assumed and the molecular flow to the surface was calculated from gas kinetic theory as:  $\varphi = (1/4)n\langle v \rangle$ , where  $n$  is the molecular density for a given CO<sub>2</sub> pressure and  $\langle v \rangle$  is the average molecular velocity at the corresponding gas temperature. Setting  $t_s = t_m$  in Eq. (4), and substituting  $t_0$  for its associated oscillation frequency,  $\nu_0 = 1/t_0$ , the activation energy for desorption can be expressed as

$$E_d = RT \ln(\nu_0 t_m). \quad (6)$$

We have taken  $\nu_0 = 2.9 \times 10^{12} \text{ s}^{-1}$  for the frequency of oscillation; this is the value used by Sandford & Allamandola (1990) and corresponds to an average of librational modes of CO<sub>2</sub>. The average values of the desorption energy obtained from the present experiments are  $E_d = 20.7 \pm 2 \text{ kJ mol}^{-1}$  for the adsorption of CO<sub>2</sub> on amorphous ice, and  $E_d = 19.9 \pm 2 \text{ kJ mol}^{-1}$  for the adsorption of CO<sub>2</sub> on crystalline ice. The  $E_d$  for crystalline ice is slightly lower (0.8 kJ mol<sup>-1</sup>) than that for amorphous ice, but the difference is small in comparison with the estimated uncertainties. Note that the uncertainty is mostly due to the assumptions made in the calculation of the  $\nu_0 t_m$  product.

The  $E_d$  value for amorphous ice obtained in the present experiments is ~15% lower than that of Sandford & Allamandola (1990) ( $E_d = 23.7 \pm 1.7 \text{ kJ mol}^{-1}$ ) which was obtained with a similar procedure. The discrepancy is not too large taking into account the respective uncertainties. There are also some differences in the experimental details. In the present study CO<sub>2</sub> was deposited on pure ice surfaces whereas Sandford and Allamandola deposited CO<sub>2</sub>/H<sub>2</sub>O mixtures. In a recent article Anderson et al. (2004) reported an activation energy  $E_d = 21.2 \pm 1.9 \text{ kJ mol}^{-1}$  for the desorption of CO<sub>2</sub> from crystalline ice. This value, obtained from time-resolved molecular beam measurements, is slightly larger (~6.5%) than ours, but both lie within the mutual experimental uncertainty. The agreement is reassuring taking into account the different experimental methods used. The molecular beam experiments of Anderson et al. (2004) also show that the interaction of CO<sub>2</sub> with amorphous ice is more complex than that with crystalline ice. This observation is in agreement with the results of the present study discussed above.

## 4. Conclusions

The main contributions of this work are related to the fact that the systems under consideration are studied simultaneously using two different techniques, with results that complement each other. In addition, we have dealt with four different types of samples corresponding to four different deposition schemes, at temperatures between 80 and 190 K, whereas in previous studies a more reduced set of data was employed. In particular, our water layers deposited at 80 K are expected to have a higher density than those of the previous TPD studies on the H<sub>2</sub>O/CO<sub>2</sub> system. Collings et al. (2004) worked with sequentially deposited and co-deposited samples formed at very low temperature (8–10 K), and heated at a slower pace of 0.08 K s<sup>-1</sup>. Their TPD experiments are carried out for concentrations of about 5% of the guest molecule in water, fairly similar to our H<sub>2</sub>O/CO<sub>2</sub> ratio of ~15/1. The reasons for the temperature discrepancies between the results of Collings et al. and those of the present work and of other authors (Bar-Nun et al. 1985; Hudson & Donn 1991) are not entirely clear but might be related to the different density of the ices formed and to the different heating rate of the desorption experiences. It is conceivable that a higher porosity, as expected from a lower temperature deposition, and a slower

heating pace, which may allow more pores to open per unit of time, permit embedded CO<sub>2</sub> to escape at lower temperatures in the experiment of Collings et al. (2004). More systematic studies of desorption as a function of deposition conditions would certainly be worthwhile.

We have also carried out experiments at smaller CO<sub>2</sub> concentrations, but the results simply change proportionally to the relative concentration of the species, and therefore are not commented on in this paper.

The experiments of Kumi et al. (2006) were carried out on sequentially deposited samples at lower exposure pressures, but the general conclusions are similar to those of the present investigation. The new evidence put forward in this study correspond to co-deposition and crystalline deposition experiments. Our co-deposition results provide increased data on the formation of a second CO<sub>2</sub> structure associated with ASW. Also, we present new evidence in the region of the  $\nu_3$  band of the <sup>13</sup>C isotopomer. The vibration of <sup>13</sup>CO<sub>2</sub>-ext, at 2282 cm<sup>-1</sup>, is seen only at 80 K, just as in sequential deposition traces, but the corresponding vibration of <sup>13</sup>CO<sub>2</sub>-int, although very weak, can be detected with a shift of ~7 cm<sup>-1</sup> after heating to 105 K.

We also provide here an estimate of the activation energies for the desorption of CO<sub>2</sub> from surfaces of amorphous ( $E_d = 20.7 \pm 2$  kJ mol<sup>-1</sup>) and crystalline water ice ( $E_d = 19.9 \pm 2$  kJ mol<sup>-1</sup>), which are in reasonably good agreement with the previous results by Sandford & Allamandola (1990) and by Anderson et al. (2004) respectively.

Sandford & Allamandola (1990) worked with co-deposited samples of quite different concentrations, including also samples with methanol. They observed large changes in wavenumber and width of the CO<sub>2</sub> vibrations, on heating from 10 to 150 K, and associated these changes with the relative concentrations of CO<sub>2</sub> and water. Our results seem to show two slightly different CO<sub>2</sub> structures, which prevail depending not only on the temperature but also on the deposition method, even for similar temperatures. We have also shown that CO<sub>2</sub> can become attached to crystalline water ice at 80 K, although it completely escapes on heating to 105 K. These findings have astronomical relevance, especially for icy bodies of the Solar System. For example, for cometary nuclei, the two different varieties of CO<sub>2</sub>-water association might have some influence in their thermophysical evolution. The spectroscopic differences due to the deposition method are also important for the characterization of the formation and evolution of cometary nuclei, and especially, of transneptunian objects, which have been found to contain both crystalline and amorphous water ices.

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