

Profile of the CO₂ bands produced after ion irradiation of ice mixtures

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Abstract. We have studied the infrared spectral characteristics of frozen carbon dioxide (CO₂) formed after ion irradiation of several astrophysically relevant ice mixtures at 10 K. Carbon dioxide is in fact readily produced by ion irradiation of icy samples of CO, and CH₃OH and mixtures H₂O:CO, CO:O₂, CO:N₂, H₂O:CH₃OH, H₂O:CH₄, H₂O:CH₄:NH₃. We have studied the profile (shape, width and peak position) of the CO₂ bands as a function of initial mixture, irradiation dose and warming up temperature.

Key words: ISM: molecules – dust, extinction – infrared: ISM: lines and bands

1. Introduction

Ground-based, air-borne and space infrared observations have clearly shown the presence of absorption features (e.g., at 3.1, 4.27, 4.67, 4.9, 6.0, 6.8, 15.2 μm) along the line of sight of embedded young stellar objects and field stars obscured by dense molecular clouds. These features are characteristic of simple molecules such as H₂O, CO₂, CO, OCS in the solid state. These molecules are believed to be frozen in icy grain mantles formed by accretion (e.g., CO) and reaction of gas phase species (e.g., H₂O) onto preexisting refractory grain cores.

Homonuclear species such as O₂ and N₂ cannot be easily directly detected by infrared spectroscopy. Their presence could be evidenced by the effects induced on the profile of other species, such as CO, and/or by the presence of new species formed after energetic processing of ice mantles by UV and/or ion irradiation (Elsila et al. 1997; Strazzulla et al. 1997). However Ehrenfreund et al. (1992) showed that in a solid matrix the transition of O₂ molecules gets weakly infrared active due to the perturbation by the surrounding species.

On the basis of laboratory experiments and theoretical calculations it had been possible to predict the presence of solid CO₂ in ice grain mantles (Tielens & Hagen 1982; d’Hendecourt et al. 1985). However because of telluric absorption its detection is

impossible with ground and airborne telescopes. D’Hendecourt & Jourdain de Muizon (1989) have reported the observation of the CO₂ bending mode at about 15.2 μm with the low resolution spectrometer of the Infrared Astronomical Satellite (IRAS). Recently new observations with the Infrared Space Observatory (ISO) have clearly shown the presence of solid CO₂ in icy grain mantles (de Graauw et al. 1996; Gürtler et al. 1996). It has been estimated that the CO₂ abundance is $\sim 15\%$ relative to H₂O.

Carbon dioxide is not predicted to have appreciable abundance in the gas phase in dense clouds so that its condensation on interstellar grains can be neglected (e.g., Whittet & Walker 1991) while its presence may be due to reaction of gas phase species on grain cores or to energetic processing such as UV and cosmic ray irradiation. Indeed, laboratory experiments have shown that CO₂ is produced after UV and ion irradiation of astrophysically relevant ices (e.g., Hagen et al. 1979; Gerakines et al. 1996; Moore et al. 1983; Palumbo & Strazzulla 1993; Strazzulla et al. 1997).

A detailed study of the profile of the CO₂ bands in different ice mixtures has already been done (Sandford & Allamandola 1990; Ehrenfreund et al. 1996). In this paper, we present a new detailed study of the profile of the two main CO₂ bands due to the asymmetric stretching mode, at about 2340 cm⁻¹ (4.27 μm), and to the bending mode at about 660 cm⁻¹ (15.2 μm) respectively, produced after ion irradiation as a function of irradiation dose, initial mixture, and warm-up history.

In order to estimate the abundance of solid CO₂ in laboratory mixtures and along the line of sight of molecular clouds, it is necessary to know the integrated absorbance value of the CO₂ bands. Different values have been reported in the literature. Yamada & Person (1964) estimated the integrated absorbance of polycrystalline CO₂ at 80 K which values 7.6 $\times 10^{-17}$ cm/molecule for the asymmetric stretching mode at about 2340 cm⁻¹ and 1.28 $\times 10^{-17}$ cm/molecule for the bending mode at about 660 cm⁻¹. Allamandola et al. (1988) assumed for the integrated absorbance of pure CO₂ the same values estimated by Sandford et al. (1988) for a H₂O:CO₂=20:1 mixture at 10 K, that is 20 $\times 10^{-17}$ cm/molecule and 4 $\times 10^{-17}$ cm/molecule for the stretching and bending mode respectively. Then Gerakines et al. (1995), assuming the absorbance values

estimated by Yamada & Person (1964) still valid at 14 K, have shown that these only weakly depend on the ice composition.

2. Experimental apparatus

A detailed description of the experimental apparatus used can be found elsewhere (Strazzulla & Baratta 1991; Spinella et al. 1991).

A stainless steel vacuum chamber ($P < 10^{-7}$ mbar) is faced to a spectrometer ($4400\text{--}400\text{ cm}^{-1} = 2.27\text{--}25\text{ }\mu\text{m}$) through KBr windows. The gas or gas mixture to be investigated is injected into the chamber through a needle valve and subsequently frozen onto a silicon crystal substrate that is in thermal contact with a cold finger (10–300 K). All of the spectra shown in the following are ratioed to a background spectrum of the silicon wafer and have been taken at resolution of 2 cm^{-1} .

Samples can be bombarded by 1.5–60 keV ions. These are obtained from an ion gun (3 kV) or an ion implanter (30 kV). From this latter double ionized Ar beams (60 keV) can be obtained. In this paper irradiation experiments with 3 keV He⁺, 30 keV H⁺, He⁺, and Ar⁺, and 60 keV Ar⁺⁺ are presented. The beam used produces current densities in the range of several 10^{-1} to a few $\mu\text{A cm}^{-2}$ in order to avoid macroscopic heating of the target. The substrate plane forms and angle of 45 degree with the IR beam and the ion beam. Thus before, during and after irradiation, spectra can be taken without tilting the sample. The energy released to the sample by impinging ions (dose) is given in eV per small molecule (16 a.m.u.) because this is a convenient way to characterize chemical changes and compare the results obtained irradiating different samples.

3. Results

As already well known, the mid-infrared spectrum of pure carbon dioxide (CO₂) ice at 10 K shows five active bands at 3708 cm^{-1} ($2.70\text{ }\mu\text{m}$; combination mode), 3600 cm^{-1} ($2.78\text{ }\mu\text{m}$; combination mode), 2343 cm^{-1} ($4.27\text{ }\mu\text{m}$; ¹²CO₂ asymmetric stretching mode), 2283 cm^{-1} ($4.38\text{ }\mu\text{m}$; ¹³CO₂ asymmetric stretching mode), 660 and 655 cm^{-1} (15.15 and $15.27\text{ }\mu\text{m}$; bending modes). Full Width at Half Maximum (FWHM) measured on percent transmission spectra of the asymmetric stretch values 16.5 cm^{-1} while for the unseparated bending doublet values 10 cm^{-1} (Sandford & Allamandola 1990).

Laboratory experiments have shown that CO₂ is formed after energetic processing (UV and ion irradiation) of C-bearing and O-bearing ice mixtures (Hagen et al. 1979; Gerakines et al. 1996; Moore et al. 1983; Palumbo & Strazzulla 1993; Strazzulla et al. 1997). In this section we present a new detailed study of the profile of the asymmetric stretching mode and the bending mode of CO₂ produced after ion irradiation of pure CO and CH₃OH and CO:O₂, CO:N₂, H₂O:CO, H₂O:CH₃OH, H₂O:CH₄, H₂O:CH₄:NH₃ mixtures.

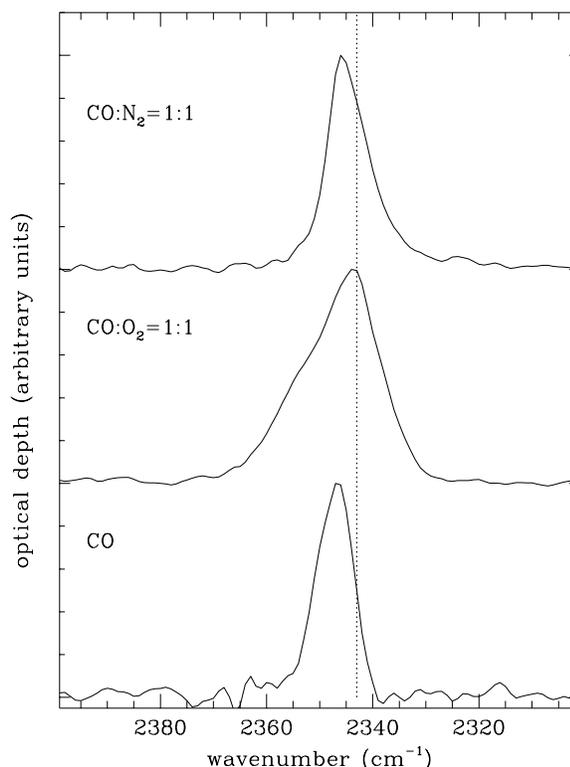


Fig. 1. The profile of the CO₂ asymmetric stretching mode, at about 2340 cm^{-1} ($4.27\text{ }\mu\text{m}$) produced after ion irradiation of non polar mixtures at 10 K. Pure CO has been irradiated with 3 keV He⁺ ions while the mixtures have been irradiated with 60 keV Ar⁺⁺ ions. The irradiation dose for all samples is $\sim 20\text{ eV}/16\text{amu}$. A dotted line at 2343 cm^{-1} , which indicates the peak position of pure CO₂ (Sandford & Allamandola 1990), has been drawn for reference.

3.1. The asymmetric stretching mode

Fig. 1 shows the profile of the CO₂ asymmetric stretching mode produced after ion irradiation of non polar mixtures (CO, CO:O₂=1:1, CO:N₂=1:1). The CO spectrum shown refers to a sample irradiated with 3 keV He⁺ at about $20\text{ eV}/16\text{amu}$; both mixtures shown have been irradiated with 60 keV Ar⁺⁺ at about $20\text{ eV}/16\text{amu}$. A dotted line at 2343 cm^{-1} , which indicates the peak position of pure CO₂ (Sandford & Allamandola 1990), has been drawn for reference.

Fig. 2 shows the profile of the CO₂ band produced after ion irradiation of polar mixtures (H₂O:CO=10:1, CH₃OH, H₂O:CH₃OH and H₂O:CH₄ at different abundance ratios, H₂O:CH₄:NH₃=2.5:2:1). Ice mixtures with methanol shown have been irradiated with 3 keV He⁺ at $\sim 40\text{ eV}/16\text{amu}$; H₂O:CO and H₂O:CH₄=1:1 mixtures shown have been irradiated with 3 keV He⁺ at $\sim 20\text{ eV}/16\text{amu}$; H₂O:CH₄=2:1 and H₂O:CH₄:NH₃=2.5:2:1 mixtures shown have been irradiated with 30 keV He⁺ at $\sim 80\text{ eV}/16\text{amu}$.

Table 1 reports peak position and FWHM (measured in an optical depth scale) of the 2340 cm^{-1} band for different initial mixtures at different irradiation doses. From these data it is possible to draw some general conclusions. The CO₂ band produced in non polar mixtures (upper part of Table 1) peaks at

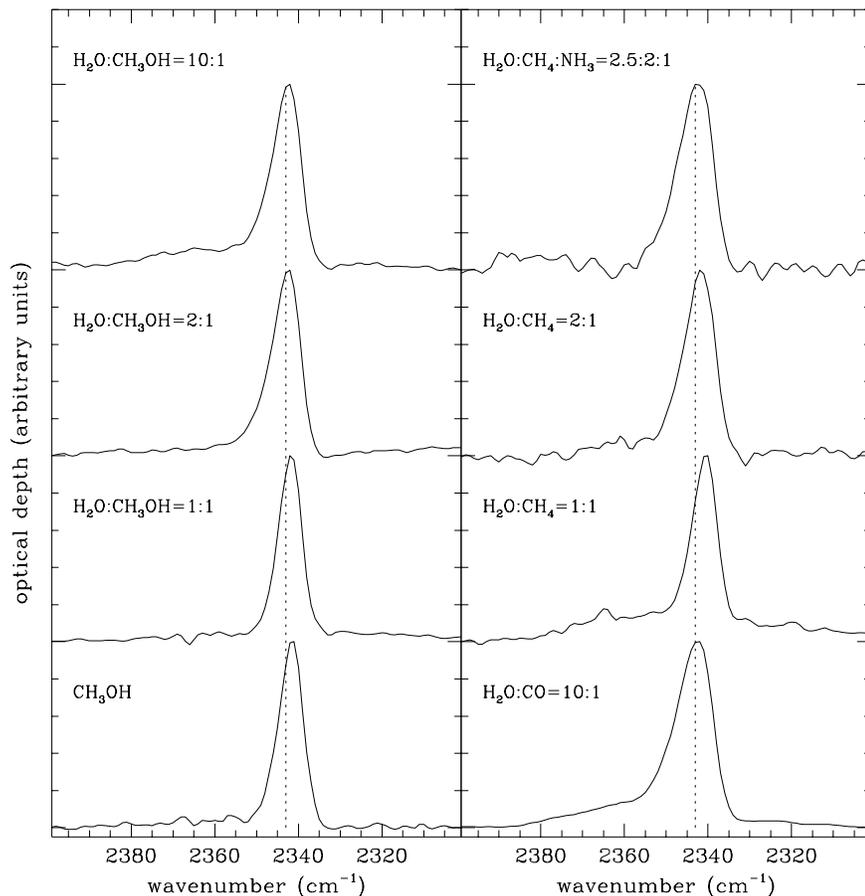


Fig. 2. The profile of the CO₂ asymmetric stretching mode, at about 2340 cm⁻¹ (4.27 μm) produced after ion irradiation of polar mixtures at 10 K. Mixtures have been irradiated with 3 keV He⁺ or 30 keV He⁺ ions. The irradiation doses range between 20 to 80 eV/16amu. A dotted line at 2343 cm⁻¹, which indicates the peak position of pure CO₂ (Sandford & Allamandola 1990), has been drawn for reference.

higher wavenumbers with respect to pure CO₂ ice while when produced in polar mixtures (lower part of Table 1) it peaks at lower wavenumbers very close to the position of pure CO₂ ice. Then, at the lower doses the band is narrow but FWHM increases as the irradiation dose increases. It is also interesting to note that after ion irradiation the structure of the ice is modified and other species than CO₂ are formed in the mixture. Both these facts affect the profile of the CO₂ bands and then it is not possible to compare the profile of the CO₂ bands produced after ion irradiation with that of the appropriate codeposited mixture because it is not possible to obtain the appropriate mixture without irradiation. As an example, Strazzulla et al. (1997, Fig. 5) have shown the amount of CO, CO₂ and suboxides present in the sample after ion irradiation of CO, CO:O₂ and CO:N₂ ice mixtures as a function of irradiation dose. In that case it is evident that the CO/CO₂ abundance ratio decreases, as the irradiation dose increases, to a value of about CO:CO₂=3:1 at the highest dose studied (71 eV/16amu). However the amount of carbon locked up in these molecules is only about 8% of the initial carbon (i.e. CO) deposited. As discussed in detail in Strazzulla et al. (1997) most of the original oxygen leave the target during irradiation while most of the carbon form a progressively carbon-rich residue in which ice species are trapped. The same applies to the polar mixtures discussed in this paper but with an organic residue replacing suboxides.

3.2. The bending mode

A band at about 660 cm⁻¹ attributed to the bending mode of solid CO₂ is also formed after ion irradiation of ice mixtures listed in Table 1. However a fully detailed study of this band is not straightforward because we have made most of the experiments with very thin films and the band due to the bending mode appears weak and is often superposed to other bands such as the libration mode of H₂O.

Fig. 3 shows the profile of the CO₂ bending mode produced after ion irradiation at 10 K of CO, CO:O₂, CO:N₂ mixtures. The CO spectrum shown refers to a sample irradiated with 30 keV He⁺ at about 12 eV/16amu; the CO:O₂ mixture has been irradiated with 3 keV He⁺ at about 11 eV/16amu; the CO:N₂ mixture with 30 keV Ar⁺ at about 20 eV/16amu. The profiles of the bending mode produced after ion irradiation have peak position and FWHM equal to 660 cm⁻¹ and 6.5 cm⁻¹ (CO), 662 and 659 cm⁻¹ and 10 cm⁻¹ (CO:O₂), 661 cm⁻¹ and 7.5 cm⁻¹ (CO:N₂).

Fig. 4 shows the profile of the CO₂ bending mode produced after ion irradiation at 10 K of CH₃OH, H₂O:CH₃OH=2:1 and H₂O:CO=10:1 mixtures. All mixtures have been irradiated with 3 keV He⁺ at about 40 eV/16amu (CH₃OH), 70 eV/16amu (H₂O:CH₃OH=2:1), and 18 eV/16amu (H₂O:CO=10:1).

Table 1. Peak position and FWHM (measured in an optical depth scale) of the CO₂ asymmetric stretching mode produced after ion irradiation of several ice mixtures both non polar (upper part) and polar (lower part).

initial mixture	dose (eV/16amu)	peak position (cm ⁻¹)	FWHM (cm ⁻¹)	
pure CO ^a	2	2346	4	
	8	2346	5	
	12	2346	7	
	21	2347	9	
	43	2345	15	
CO:O ₂ =1:1 ^a	71	2345	17	
	4	2345	6	
	10	2344	10	
	11	2344	12	
	23	2344	16	
CO:N ₂ =1:1 ^a	59	2343	22	
	1	2347	5	
	5	2346	6	
	13	2346	8	
	26	2346	9	
H ₂ O:CO=10:1	66	2346	14	
	8	2343	10	
	18	2342	11	
	pure CH ₃ OH	16	2341	6
		20	2341	7
24		2341	7	
40		2341	9	
H ₂ O:CH ₃ OH=1:1	44	2342	6	
	H ₂ O:CH ₃ OH=2:1	40	2342	8
		70	2342	10
H ₂ O:CH ₄ =1:1	20	2340	8	
	52	2342	9	
H ₂ O:CH ₄ =2:1	20	2341	8	
	40	2341	8	
	80	2342	9	
H ₂ O:CH ₄ :NH ₃ 2.5:2:1	40	2343	8	
	80	2343	9	
	120	2342	10	

^a Strazzulla et al. (1997)

3.3. Warm-up effects

For most of the ice mixtures listed in Table 1 we have studied the effects induced by warm-up. Table 2 reports peak position and FWHM (measured in an optical depth scale) of the asymmetric stretch produced after ion irradiation at 10 K and warmed-up. As general results, it is possible to note that peak position shifts to lower wavenumbers while FWHM decreases as temperature increases. The same effects have been reported for unirradiated mixtures by Sandford & Allamandola (1990).

Fig. 5 shows the profiles of the 2340 cm⁻¹ band produced after ion irradiation (10 K) of a H₂O:CH₃OH=2:1 mixture at two different doses and warmed up to 100 and 160 K. It is interesting to note that between 10 and 100 K peak intensity increases, FWHM decreases while the integrated intensity (i.e., the band area) is constant.

Table 2. Peak position and FWHM (measured in an optical depth scale) of the CO₂ asymmetric stretching mode after warm-up of ion irradiated ice mixtures.

initial mixture	T (K)	peak position (cm ⁻¹)	FWHM (cm ⁻¹)
CH ₃ OH +40 eV/16amu	10	2341	9
	50	2341	9
	100	2341	9
	150	2340	9
H ₂ O:CH ₃ OH=2:1 +40 eV/16amu	10	2342	8
	50	2342	7
	100	2341	6.5
	160	2340	11 ^a
H ₂ O:CH ₃ OH=2:1 +70 eV/16amu	10	2342	10
	100	2341	8
	160	2338	7.5
H ₂ O:CH ₄ =2:1 +80 eV/16amu	10	2342	9
	50	2341	9
	100	2340	8
	150	2339	7.5
H ₂ O:CH ₄ :NH ₃ =2.5:2:1 +120 eV/16amu	170	2338	7.5
	10	2342	10
	50	2342	10
	100	2341	9
	150	2340	8.5

^a including a shoulder

Sandford & Allamandola (1990) report that in a H₂O:CH₃OH:CO₂=20:10:1 mixture warmed-up to 140 K a new band grows near 2346 cm⁻¹ while the band near 2340 cm⁻¹ decreases. The intensity of the new band is greater than the other band. They suggest that the ice anneals into a crystalline form containing a substantial number of larger sites involving CH₃OH in which the CO₂ is trapped.

The present results (Fig. 5) indicate that the behaviour of the profile of the 2340 cm⁻¹ band is different if produced in a H₂O:CH₃OH mixture after irradiation and in turns depends on the irradiation dose. The lower panel of Fig. 5 shows that between 100 and 160 K the peak intensity decreases, indicating that some CO₂ has sublimated, and a new weak band appears near 2345 cm⁻¹. This band is not present in the spectrum taken at the same temperature of a mixture irradiated at higher dose (upper panel) and in this latter case less CO₂ has sublimated with respect to the initial amount at 10 K. This shows that after ion irradiation the structure of the ice is different and crystallization as well as sublimation temperature change with respect to an unirradiated mixture (see Sandford and Allamandola 1990).

The behaviour of the bending mode after warm-up is similar to that of the stretching mode described above. Again peak intensity increases and peak position slightly shifts as the temperature increases. Fig. 6 shows the profile of the CO₂ band produced after ion irradiation of CO at 10 K (12 eV/16amu; dashed line) and after warm-up to 40 K. At 40 K the irradiated CO has sublimated while suboxides formed after ion irradiation as well are left over (Brucato et al. 1997). The band at 40 K shown in the figure is attributed to CO₂ trapped in the suboxides matrix and in fact is different from that of pure CO₂.

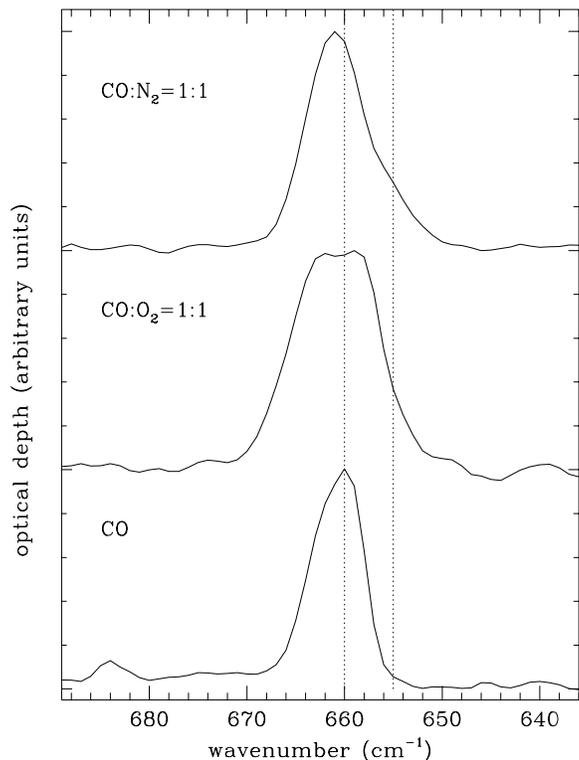


Fig. 3. The profile of the CO₂ bending mode, at about 660 cm⁻¹ (15.1 μm) produced after ion irradiation of non polar mixtures at 10 K. Mixtures have been irradiated with 3 and 30 keV He⁺ and 30 keV Ar⁺ ions. The irradiation doses range between 10 to 20 eV/16amu. Dotted lines at 660 cm⁻¹ and 655 cm⁻¹, which indicate the peak position of pure CO₂ (Sandford & Allamandola 1990), have been drawn for reference.

Also a weak feature (not shown) attributed to a small fraction of trapped CO is present in the same spectrum.

4. Discussion

Laboratory experiments and theoretical calculations had predicted and ISO observations have confirmed the presence of solid carbon dioxide in icy grain mantles. However the origin of solid CO₂ is not yet clear. Carbon dioxide is not predicted to have appreciable abundance in the gas phase in dense clouds so that its condensation on interstellar grains can be neglected (e.g., Whittet & Walker 1991). Thus its presence may be due to reaction of gas phase species on grain cores or to energetic processing such as UV and cosmic ray irradiation. Indeed, laboratory experiments have shown that CO₂ is produced after UV and ion irradiation of astrophysically relevant ices (Hagen et al. 1979; Gerakines et al. 1996; Moore et al. 1983; Palumbo & Strazzulla 1993; Strazzulla et al. 1997). However the amount of CO₂ produced after UV or ion irradiation of the same initial mixture can be different. As an example, after 1 hour UV irradiation of CO the N(CO)/N(CO₂) ratio values ~80 (Gerakines et al. 1996) while after ion irradiation this ratio values ~10 at a dose that we have estimated equivalent to 1 hour UV irradiation.

In this paper we have presented a detailed study of the profile of the main CO₂ bands (stretching mode at about 2340 cm⁻¹

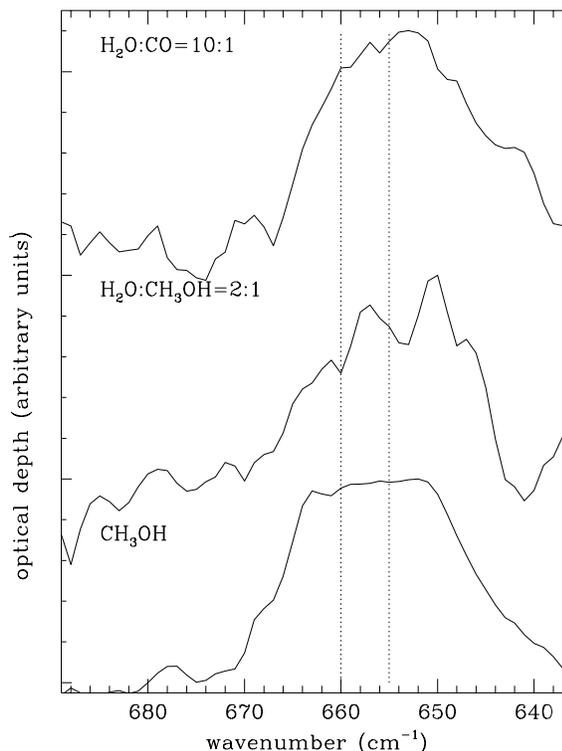


Fig. 4. The profile of the CO₂ bending mode, at about 660 cm⁻¹ (15.1 μm) produced after ion irradiation of polar mixtures at 10 K. Mixtures have been irradiated with 3 keV He⁺ ions. The irradiation doses range between 20 to 70 eV/16amu. Dotted lines at 660 cm⁻¹ and 655 cm⁻¹, which indicate the peak position of pure CO₂ (Sandford & Allamandola 1990), have been drawn for reference.

and the bending mode at about 660 cm⁻¹) produced after ion irradiation of some C- and O-bearing ices. We have shown that band profiles depends on the initial mixture, irradiation dose and warm-up.

Preliminary comparisons of laboratory spectra of icy mixtures containing CO₂ with the ISO spectra (de Graauw et al. 1996) have shown that it is not possible to find a single spectrum which fits the CO₂ observed bands and it has been suggested that the observed features are due to the sum of independent components. However the mixtures which fit simultaneously both CO₂ bands (i.e. the stretching and the bending modes) have not yet been found. It is interesting to note that as far as we know ISO data (e.g. de Graauw et al. 1996; Gürtler et al. 1996) show that peak position and FWHM of the CO₂ stretching mode range between 2342 and 2345 cm⁻¹ and 17 and 26 cm⁻¹ respectively. These peak positions fall within values reported in Table 1 while widths are larger than that obtained in the laboratory as expected if the observed bands are due to the sum of independent components.

When ISO data are available to the scientific community it will be possible to compare them directly with our laboratory spectra following a procedure similar to that used to compare the observed interstellar solid CO bands with laboratory data (e.g., Palumbo & Strazzulla 1993; Teixeira et al. 1998). Then

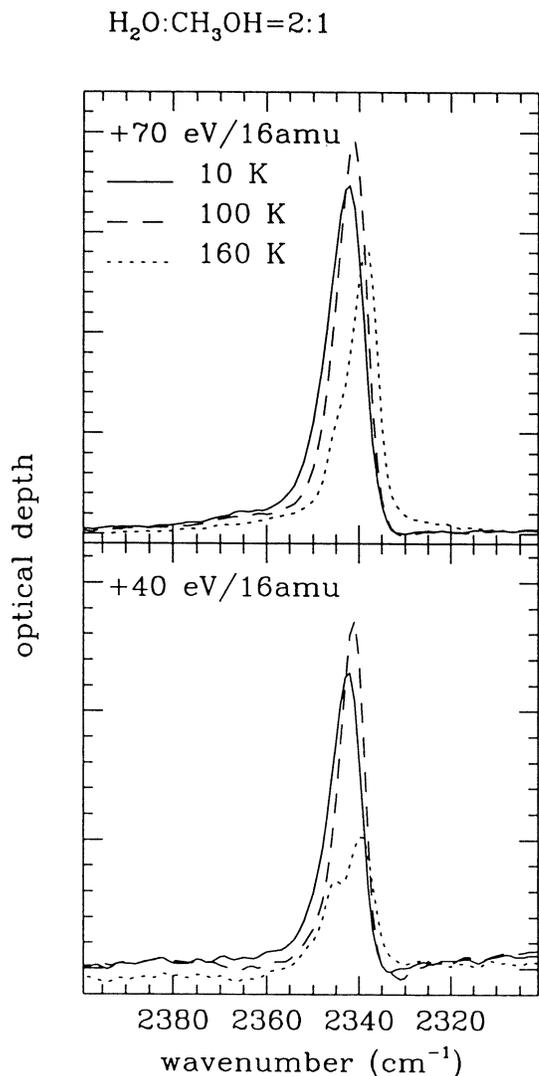


Fig. 5. The profile of the CO₂ stretching mode produced after ion irradiation at 10 K (solid lines) of a H₂O:CH₃OH=2:1 mixture with 40 eV/16amu (lower panel) and 70 eV/16amu (upper panel). In both panels dashed lines and dotted lines show the profile of the same band after warmup to 100 K and 160 K respectively.

the main challenge will be to obtain a comparison of both solid CO and CO₂ interstellar bands with the same laboratory spectra.

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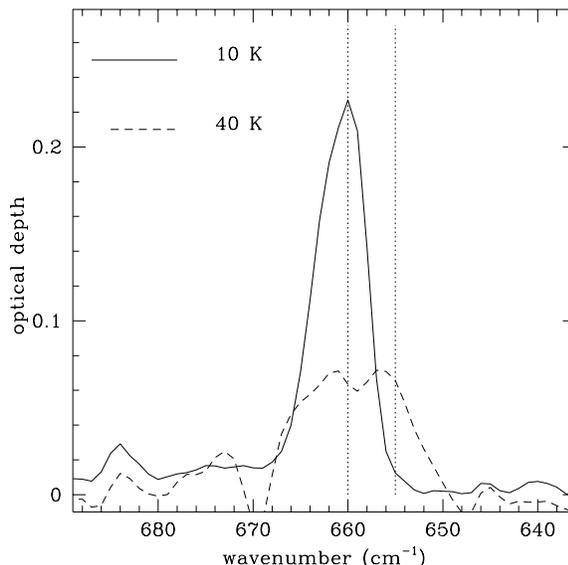


Fig. 6. The profile of the bending mode of CO₂ produced after ion irradiation of CO at 10 K (12 eV/16amu; solid line) and after warm-up to 40 K (dashed line). This latter spectrum taken after CO has sublimated shows the profile of CO₂ left over and trapped in the suboxides matrix.

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