Laboratory and astronomical IR spectra: an experimental clue for their comparison

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Abstract. It is well known that particle shape and size can have very important effects on the profile of icy absorption features. In fact Mie-scattering calculations show that absorption features can be shifted with respect to laboratory (bulk) spectra of thin films and subpeaks appear. The difference between bulk spectra and small particle extinction spectra depends on the optical constants (n, k) of the sample and in particular it is not negligible for those species with "strong transitions" and at high concentration in the ice mixture. In order to know whether a band profile in a specific ice mixture would be affected by particle shape and size effects it is necessary to have the optical constants of that mixture and perform small particles cross-section calculations. However if in principle optical constants can always be measured in practice this is not straightforward. After several years of experiments and IR spectroscopy of icy mixtures we have found an experimental method to know whether particle shape and size would affect the profile of an absorption feature and hence whether laboratory spectra of thin films are representative of small particles extincion spectra. In particular, we have found that some instances exist in laboratory spectra for which the profile of absorption bands depends on the inclination of the ice film with respect to the infrared beam of the spectrometer. Furthermore when this is the case if the spectrum is taken at oblique incidence the band profile depends on the polarization of the infrared beam as well. Here we show that when a band profile in a laboratory spectrum depends on the inclination of the sample or, equivalently, on the polarization of the electric vector of the IR beam this cannot be directly compared to astronomical observations.

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

1. Introduction

Infrared spectra (2–25 μm) of obscured sources such as deeply embedded protostars and field stars, clearly show absorption features superposed to the continuum (e.g., 3.1, 4.27, 4.67, 6.0, 6.8, 9.7, 15.2 μm). These features are characteristic of species

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in solid form and their identification has been mainly based throughout the years on the comparison with laboratory spectra. Apart from the features due to the silicates in interstellar grains the others are attributed to frozen molecules i.e., icy mantles which form on interstellar grains in dense molecular clouds. The comparison with laboratory spectra of thin icy films has often been successful and several molecules have been firmly identified such as H_2O (Hagen et al. 1980), CO (Lacy et al. 1984; Tielens et al. 1991; Chiar et al. 1994, 1995; Teixeira et al. 1998), CO_2 (de Graauw et al. 1996; Gerakines et al. 1999), OCS (Palumbo et al. 1995, 1997), CH_4 (Lacy et al. 1991; Boogert et al. 1996, 1997), CH_3OH (Tielens & Allamandola 1987; Allamandola et al. 1992; Dartois et al. 1999). However it is well known that particle size and shape can have very important effects on the profile (shape, width and peak position) of absorption features. For strong transitions in small particles this class of electromagnetic modes is referred to as "surface modes" (van de Hulst 1957; Bohren & Huffman 1983). Because of surface modes absorption features can be shifted with respect to laboratory (bulk) spectra, and subpeaks appear. Mie-calculations have been performed (e.g., H_2O (Léger et al. 1983; Greenberg et al. 1983), CO (Tielens et al. 1991; Ehrenfreund et al. 1997), OCS (Palumbo et al. 1995), CO_2 (Ehrenfreund et al. 1997)) and it has been shown that when absorption band profiles are affected by "surface modes" laboratory spectra are no longer representative of the small particles extinction spectrum.

For a long time we have studied in the laboratory the infrared spectra of several icy mixtures. Here we present spectra which have been taken with the substrate plane (on which the icy sample is deposited) forming different angles (normal incidence and oblique incidence) with respect to the infrared beam of the spectrometer. Furthermore, spectra have been taken with the electric vector of the beam parallel (P polarized) and perpendicular (S polarized) to the plane of incidence. We have found that some instances exist in which the incidence angle and the polarization strongly affect the absorption band profiles. Using the optical constants measured by Baratta & Palumbo (1998) we have performed Mie scattering calculation for spherical grains. We have found that when band profiles are influenced by surface modes then they are also affected by the incidence angle and the polaritazion in the laboratory spectra. This result provide us with an experimental method to know when laboratory spectra of thin
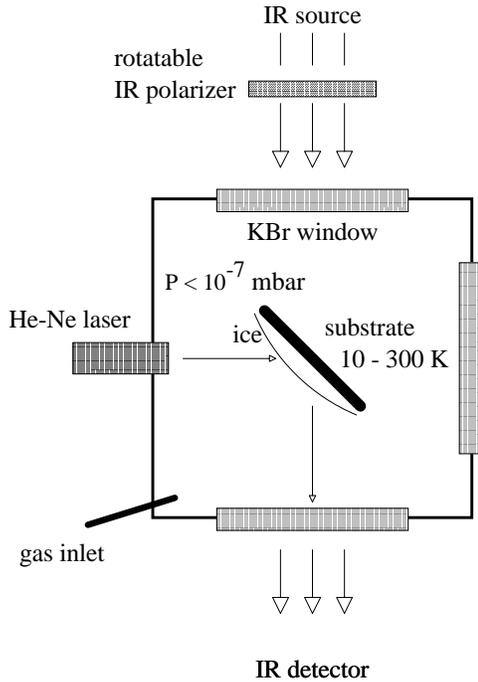
Fig. 1. Schematic view of the experimental set-up

films are representative of small particle extinction spectra and hence can be directly compared with astronomical spectra.

We describe the experimental set-up in Sect. 2; we present the laboratory results in Sect. 3 and discuss their implications in Sect. 4.

2. Experimental set-up

The infrared spectra here shown have been taken in the 4400–500 cm^{-1} (2.27–20 μm) range with a Bruker Equinox 55 FTIR spectrometer. A stainless steel vacuum chamber (shown in Fig. 1) faces the spectrometer through KBr windows. Gases are accreted by a gas inlet on a silicon (or KBr) substrate which usually is inclined of 45 degrees with respect to the infrared (IR) beam of the spectrometer. For the purposes of this paper we have also mounted a substrate inclined of 90 degrees with respect to the IR beam. In this case, the incidence angle (i.e., the angle between the IR beam and the normal to the substrate plane) is zero degrees. The substrate is put in thermal contact with a closed-cycle helium cryostat whose temperature can be varied in the 10–300 K range. In this experimental set-up (with the substrate inclined of 45 degrees) it is possible to monitor the thickness of the film during accretion, by looking at the interference pattern (intensity versus time) given by a He-Ne laser beam reflected at an angle of 45 degrees both by the vacuum-film and film-substrate interfaces. For each sample, at all the examined temperatures, two spectra with the electric vector of the infrared beam parallel (P polarized) and perpendicular (S polarized) to the plane of incidence have been taken where the polarization of the infrared radiation is changed by rotating a polarizer placed in the path of the infrared beam (Fig. 1). This polarizer can be removed in order to take unpolarized spec-

tra. All the spectra for a given polarization are ratioed to the corresponding spectrum of the background acquired before deposition. Unless when differently specified, spectra have been taken at a resolution of 1 cm^{-1} and sampling of 0.25 cm^{-1}. For a more detailed description of the experimental procedure the reader is referred to Baratta & Palumbo (1998).

3. Experimental results

Several spectra of icy samples have been taken at two different incidence angles (45 and 0 degrees) and in the two different polarizations (P and S). In some cases ("weak" transitions) absorption band profiles coincide when the angle or the polarization is changed. However some instances exist ("strong" transitions) in which the spectra strongly depend on the incidence angle and on the polarization. For example this is the case for the stretching and bending modes of solid $^{12}CO_2$, for the stretching mode of solid CO and the C-O strething mode of OCS and in general depends on the optical constants (n, k). Here we consider as an example the case for CO_2 and in particular a mixture $CH_3OH:CO_2$=1:1 and pure CO_2.

3.1. The CH$_3$OH:CO$_2$ mixture

Figs. 2 to 5 show the absorption spectrum of a $CH_3OH:CO_2$=1:1 mixture in four different ranges. The mixture has been deposited at 12.5 K and then warmed up to 105 K. In Fig. 2 the 3800–2700 cm^{-1} range is shown where the bands at about 3250 cm^{-1} and 2950 and 2830 cm^{-1} are due to the O-H stretching mode and C-H stretching modes in methanol respectively (see e.g., Sandford & Allamandola 1993); the bands at about 3600 cm^{-1} and 3700 cm^{-1} are due to combination modes of CO_2 (see e.g., Sandford & Allamandola 1990). Fig. 3 shows the 2400–2300 cm^{-1} spectral range. The band at about 2340 cm^{-1} is due to the asymmetric stretching mode of $^{12}CO_2$. Fig. 4 shows the 2300–2250 cm^{-1} region. The absorption band at about 2280 cm^{-1} is due to the asymmetric stretching mode in $^{13}CO_2$. Finally, Fig. 5 shows the 700–600 cm^{-1} region in which the absorption due to the bending mode of $^{12}CO_2$ occurs. Here we show the spectra after warm-up to 105 K however several spectra have been taken at 12.5 K and during warm-up and the results here discussed are valid at all temperatures. In all figures the top panels show two laboratory spectra taken at oblique incidence (45 degrees) and at normal incidence (0 degrees) respectively. It is evident that these two laboratory spectra are almost equal in Figs. 2 and 4 and are quite different in Figs. 3 and 5. In the middle panels the case of oblique incidence is considered and spectra have been taken in the two different polarizations (P and S). The absorption band profiles shown in Figs. 2 and 4 do not depend on the polarization of the IR beam while the profiles shown in Figs. 3 and 5 strongly depend on the polarization. In the same panels it is shown the unpolarized spectrum computed from the spectra taken in P and S polarization using the equation

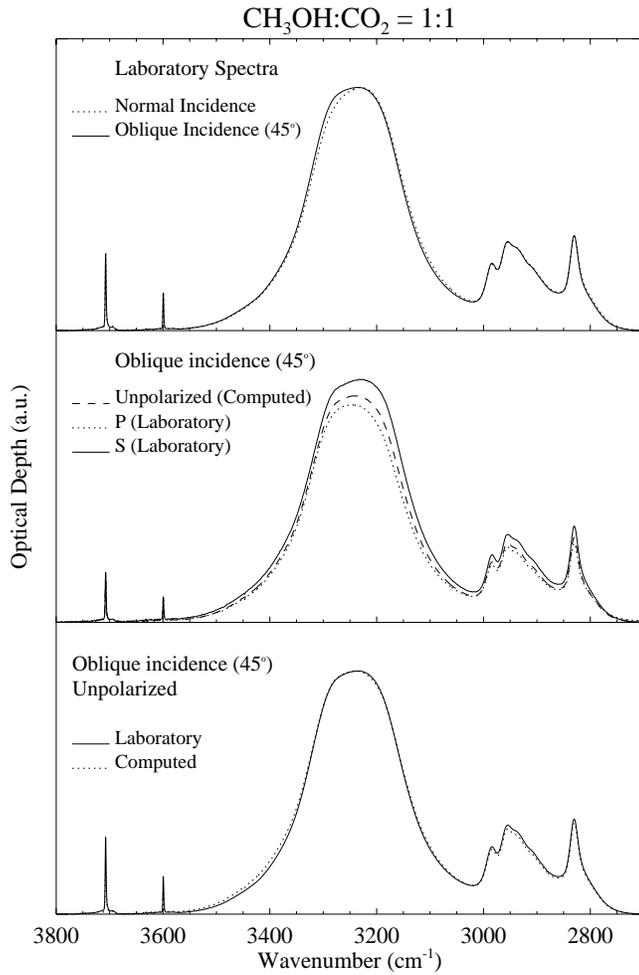$$T_U = \frac{T_P + \frac{B_S}{B_P}T_S}{1 + \frac{B_S}{B_P}} \qquad (1)$$

Fig. 2. Laboratory and computed spectra of a mixture $CH_3OH:CO_2=1:1$ in the 3800–2700 cm^{-1} spectral region. The mixture has been deposited at 12.5 K and spectra have been taken after warm-up to 105 K. The upper panel shows a comparison between the spectra taken at normal and oblique incidence. In the middle panels the laboratory spectra taken at oblique incidence in P and S polarization are compared with the computed unpolarized spectrum at the same angle. In the bottom panel the computed unpolarized spectrum is compared with the laboratory unpolarized one

Fig. 3. The same as Fig. 2 in the 2400–2300 cm^{-1} spectral region

3.2. Pure CO$_2$

Baratta & Palumbo (1998) have already shown that the laboratory spectra of pure CO_2 at 45 degrees taken in P and S polarizations differ to each other. Furthermore they have measured the optical constants (n and k) of pure CO_2 and have shown that the computed spectrum at 45 degrees perfectly compares with the laboratory spectrum taken at the same incidence angle. Using the optical constants measured by Baratta & Palumbo (1998) we have computed the absorption spectra of pure CO_2 at different incidence angles. Fig. 6 shows the calculated spectra for thin films in the region of the main absorption bands: the $^{12}CO_2$ asymmetric stretching and bending modes and the $^{13}CO_2$ asymmetric stretching mode. It is evident that for $^{12}CO_2$ the band profiles strongly depend on the incidence angle. In fact at any angle different from zero new bands appear at 2375 cm^{-1} and 675 cm^{-1} respectively whose intensity depends on the incidence angle. Baratta & Palumbo (1998) have shown that these bands are real. However they are not due to absorption (k) but to the increased reflectivity corresponding to the region across the absorption band where $n < 1$. In the bottom panel of Fig. 6 it is shown the profile of the $^{13}CO_2$ stretching mode. In this case the profile does not depend on the incidence angle but only the

which takes into account the different background spectra in the two polarizations. T_U is the unpolarized transmission spectrum, T_P and T_S are the spectra of the sample in P and S polarization respectively and B_P and B_S are the spectra of the background (which include the substrate) in P and S polarization respectively. As shown in the bottom panels the computed unpolarized spectrum at oblique incidence perfectly matches the laboratory unpolarized spectrum at the same incidence angle. Furthermore it is evident from all these figures that the spectrum at oblique incidence taken in S polarization is equivalent to the unpolarized spectrum at normal incidence. On the other hand at normal incidence the polarized spectra are always exactly equal to the unpolarized ones; in fact, due to the symmetry, in this case all the possible orientations of the electric vector are equivalent.
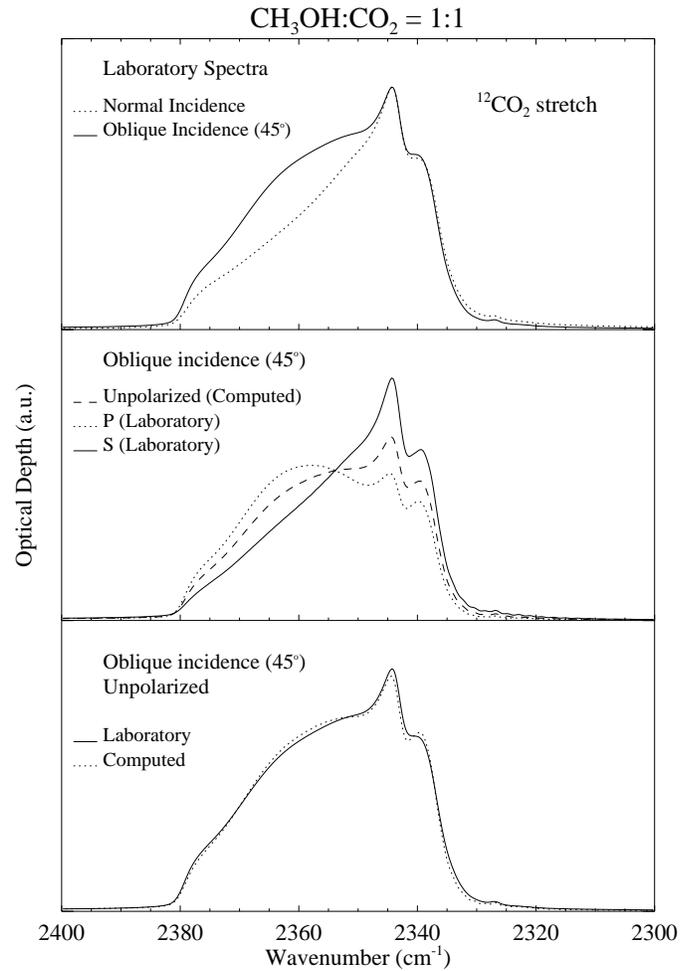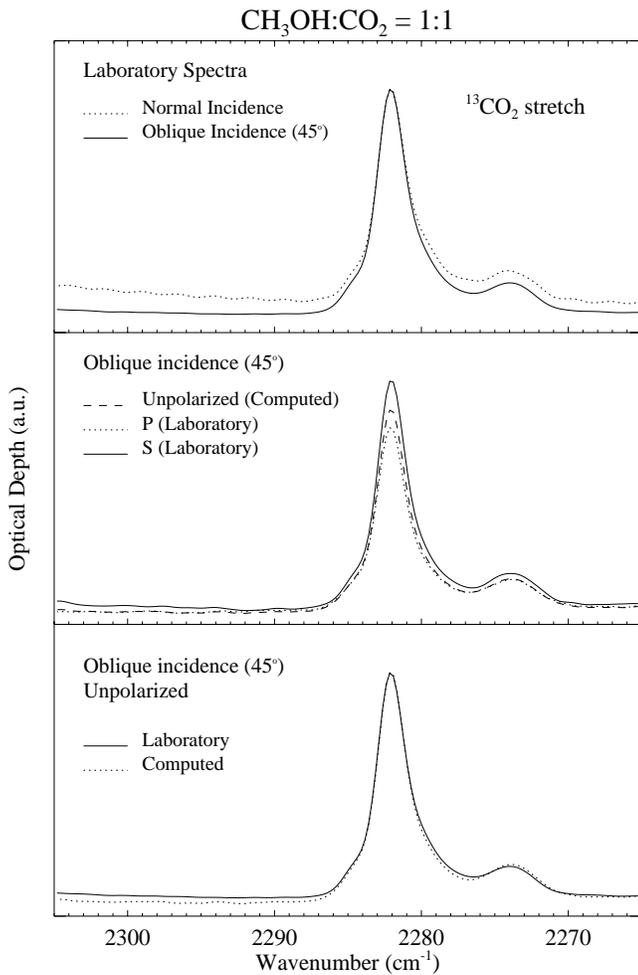
Fig. 4. The same as Fig. 2 in the 2300–2250 cm^{-1} spectral region

Fig. 5. The same as Fig. 2 in the 700–620 cm^{-1} spectral region

intensity changes due to the different path of the IR beam in the icy sample.

Using Mie theory we have calculated the extinction cross section for two different grain models: spheres and core+mantles spheres. In this latter case we have assumed that the core is made of a typical glass (dielectric) with $n = 1.6$ and $k = 0$. In the calculation we have used r_0=0.12 μm for the spheres and r_0=0.12 μm and r_1=0.1512 μm for the coated spheres (core+mantles) in such a way that the volume of the core is the same as the volume of the mantle. Results are reported in Fig. 7. We verified that in both cases the scattering cross section is negligible (particles can be considered in the Rayleigh limit). In Fig. 7 the spectra calculated using the Mie theory are compared with the synthetic spectra computed for thin films assuming normal incidence (0 degrees) and oblique incidence (60 degrees), already shown in Fig. 6. It is evident that these four spectra exactly coincide for the asymmetric stretching mode of $^{13}CO_2$ while they are quite different for the $^{12}CO_2$ bands. In particular, the core+mantle grain model shows two features at about 675 cm^{-1} in the CO_2 bending mode region and at about 2380 cm^{-1} in the CO_2 stretching mode region which are similar to the features which appears in the spectra
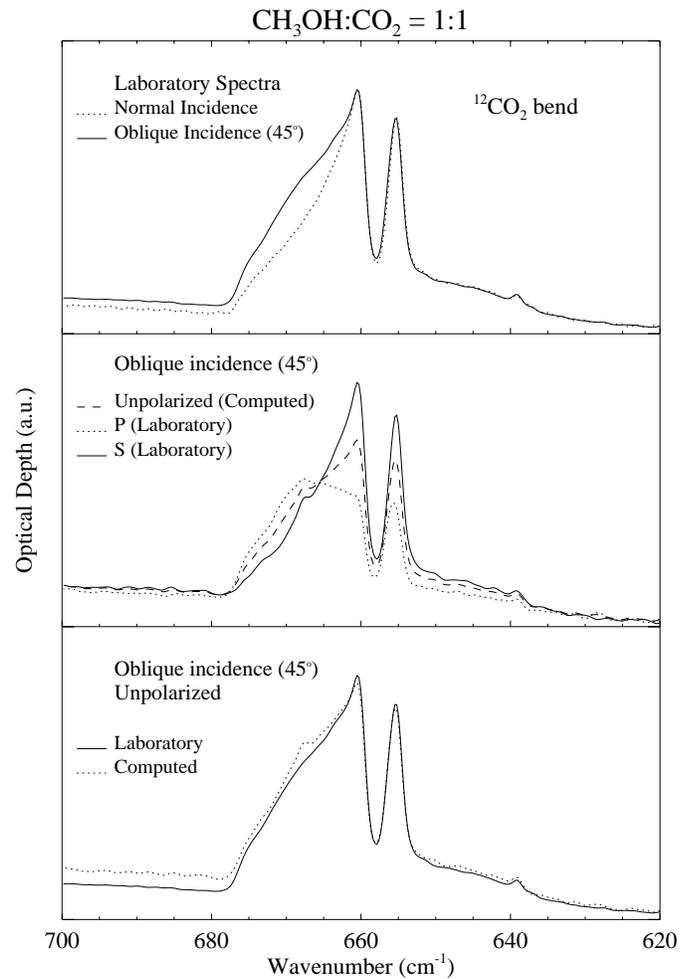
of the thin film at 45 and 60 degrees. However these features differ in position to each other. In the case of spherical grains no additional feature appears and the main peak shifts to higher wavenumbers. A discussion on the details of the origin of the features observed in small particle absorption cross section can be found in Ehrenfreund et al. (1997).

4. Discussion and conclusions

We have studied the profile of infrared absorption bands of icy films containing different molecules of astrophysical interest as a function of the incidence angle and of the polarization of the IR beam of the spectrometer. Here we have presented the results relative to the profile of CH_3OH and CO_2 absorption bands in an icy mixture $CH_3OH:CO_2$=1:1 and of pure CO_2. We have shown that in some cases the band profiles do not depend on the incidence angle or on the polarization (e.g., absorption bands due to CH_3OH in the $CH_3OH:CO_2$ mixture, asymmetric stretching mode of $^{13}CO_2$). However some instances exist in which the absorption profiles strongly depend on the incidence angle and the polarization. For example this is the case of the stretching and bending mode of CO_2. Here we have discussed the results relative to pure CO_2 and CO_2 in mixture with
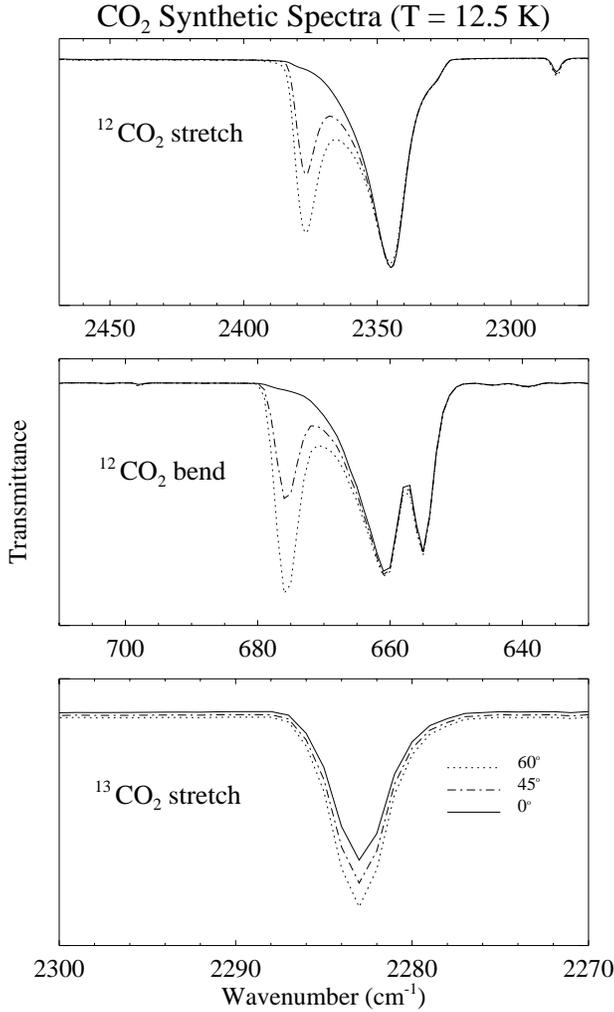
CO_2 Synthetic Spectra (T = 12.5 K)

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Fig. 6. Computed spectra of pure CO_2 in the spectral regions of the main absorption bands. The $^{12}CO_2$ stretching mode (top panel), the $^{12}CO_2$ bending mode (middle panel), the $^{13}CO_2$ stretching mode (bottom panel). The spectra have have been computed assuming normal incidence ($0°$, solid lines) and oblique incidence ($45°$, dot-dashed lines; $60°$ dotted lines

Fig. 7. Calculated absorption cross sections for homogeneous (dot-dashed lines) and coated (core+mantles, dashed lines) spheres for the main absorption bands of pure CO_2. These are compared with calculated spectra of thin films at normal incidence ($0°$, solid lines) and oblique incidence ($60°$, dotted lines)

CH_3OH. Baratta & Palumbo (1998) present the results relative to pure CO_2 and CO; Palumbo & Baratta (2000) discuss the case of CO_2 in mixture with H_2O and CH_3OH. We have compared the synthetic laboratory spectra of pure CO_2 at different incidence angle with Mie-calculated absorption cross sections. We have shown that shape and peak position of the CO_2 fundamental bands are strongly influenced by "surface modes" while for the CO_2 isotope stretching mode the laboratory measured absorption spectra give a very accurate representation of the particle extinction spectrum.

It is well known that the interaction of light with small particles can be different from that with bulk films, resulting in differences in the profile of absorption features between laboratory and interstellar spectra. In order to compare the experimental data with astronomical observations the extinction cross sections for small particles must be derived. For this purpose accurate sets of optical constants are needed. The shape and peak
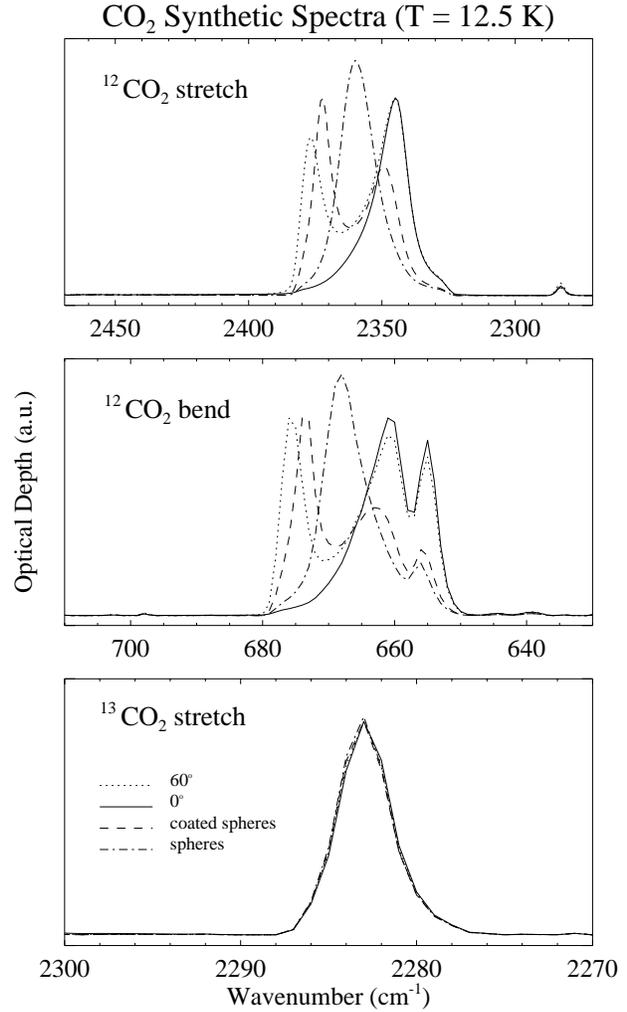
position of the bands strongly depends on the adopted model (size and grain shape). In fact small particles may give rise to multiple extinction peaks where their number and position depend on the grain shape and on the $k^2 - n^2$ value across the band (see e.g., Ehrenfreund et al. 1997). In general, the band profile will depend in a complex way on the material (n and k values) and on the geometry (size and shape for grains; incidence angle, polarization and thickness for thin films). Anyway the degree of dependence of the band profile on the geometry is related to n and k values. In particular, if the absorption feature is "weak" (small value of k and consequently, according to the K-K relation, small variation of n across the band) all these differences are faded away and all the absorption profiles will be similar independently of the grain shape and size or the incidence angle, polarization and thickness. Under these circumstances a direct comparison between transmission spectra of laboratory ice mixtures and astronomical observations is allowed. On the

other hand, if the band profile observed in a transmission spectrum of a thin film depends on the geometry (i.e., incidence angle or equivalently on P and S polarization at oblique incidence), then the laboratory spectrum differs from the extinction cross section for small particles and in addition different grain shapes give rise to different band profiles. If this is the case a direct comparison is not possible even because one should wonder which laboratory spectrum (at which incidence angle) has to be compared with astronomical observations. Unfortunately the answer is "none".

Hence from the results here shown it is possible to conclude that when the band profiles in thin films depend on the incidence angle or on the polarization then laboratory spectra are not representative of particle extinction cross section and surface modes are not negligible.

Furthermore our results show that when the optical constants of a particular icy mixtures are not known and hence small particles cross-section calculations cannot be performed, it is possible to know whether surface modes would affect the band profile experimentally, both taking the spectra in the laboratory at oblique incidence at different polarizations and taking the spectra at different incidence angle. However even if subpeaks appear in these conditions their position depend on particles shape (Ehrenfreund et al. 1997) and in turn these laboratory spectra cannot be directly compared to astronomical spectra. Quoting Bohren & Huffman (1983):"All of this illustrates a general rule, which we can state but not prove: if there is an interesting effect in a thin film, there will be a corresponding effect in small particles".

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