Crystallization of CO₂ ice and the absence of amorphous CO₂ ice in space

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Carbon dioxide (CO₂) is one of the most relevant and abundant species in astrophysical and atmospheric media. In particular, CO₂ ice is present in several solar system bodies, as well as in interstellar and circumstellar ice mantles. The amount of CO₂ in ice mantles and the presence of pure CO₂ ice are significant indicators of the temperature history of dust in protostars. It is therefore important to know if CO₂ is mixed with other molecules in the ice matrix or segregated and whether it is present in an amorphous or crystalline form. We apply a multidisciplinary approach involving IR spectroscopy in the laboratory, theoretical modeling of solid structures, and comparison with astronomical observations. We generate an unprecedented highly amorphous CO₂ ice and study its crystallization both by thermal annealing and by slow accumulation of monolayers from the gas phase under an ultrahigh vacuum. Structural changes are followed by IR spectroscopy. We also devise theoretical models to reproduce different CO₂ ice structures. We detect a preferential in-plane orientation of some vibrational modes of crystalline CO₂. We identify the IR features of amorphous CO₂ ice, and, in particular, we provide a theoretical explanation for a band at 2,328 cm⁻¹ that dominates the spectrum of the amorphous phase and disappears when the crystallization is complete. Our results allow us to rule out the presence of pure and amorphous CO₂ ice in space based on the observations available so far, supporting our current view of the evolution of CO₂ ice.

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Carbon dioxide (CO₂) has come to play a fundamental role in several aspects of the Earth's geophysics (1, 2), but it is also a key element in astrophysical research (3, 4). In the interior of dense interstellar clouds, as well as in the envelopes around young stars, dust grains are covered by ice mantles formed by frozen volatile molecules, with water being the most abundant molecular species, followed by carbon monoxide (CO), CO₂, methanol, methane, and others (5, 6). The structure of CO₂ in the icy phase of the interstellar grains is still an open question. Is CO₂ mixed up with other frozen components, or is it segregated in multilayer structures (7)? Has it attained a crystalline arrangement, or does it have an amorphous structure (8)? Because solid CO₂ is an indicator of the temperature history in the envelopes of young stars (9, 10), it is important to address these questions. Most of the available information on these systems comes from spectroscopic observations. Thus, many laboratory experiments have been performed on low-temperature CO₂, both as a single species and mixed with other components, using IR spectroscopy as the main detection tool (11–15). In the context of solid-state physics, the existence of transverse optical (TO) and longitudinal optical (LO) modes in amorphous materials was questioned because the origin of this effect was linked to long-range order in crystals, but it was proved that longitudinal modes can also propagate in amorphous media (16). We provide experimental and theoretical evidence of LO/TO splitting in the spectra of amorphous CO₂ ice.

The formation of the CO₂ observed in ice mantles is expected to occur through reactions on and in the ice matrix. These CO₂

molecules will desorb eventually, and the grains may accrete, forming new ice mantles, provided that the dust temperatures are low enough. This contribution deals with the process undergone by amorphous CO₂ when transforming to its crystalline structure. We will show that the energy delivered on the amorphous solid by heating the substrate that holds it is equivalent to that originating from the accumulation of successive layers simulating CO₂ accretion on dust, as far as the crystallization process is concerned, although complete crystallization is only reached after thermal annealing. Our tools are different varieties of IR spectroscopy supported by computer models of both amorphous and crystalline CO₂. Our materials are slowly grown ices of CO₂ at cryogenic temperatures as low as 8 K and with an ultrahigh vacuum. At the same time, we propose answers to two specific questions often raised in the astrophysics and ice physics communities: How can we distinguish between pure and amorphous CO₂ ice from the observed spectra of ice mantles, and what is the expected appearance of LO modes in the spectra of amorphous CO₂ ice?

Results and Discussion

We first present the results obtained with the new Interstellar Astrochemistry Chamber (ISAC) at the Center of Astrobiology (CAB) (17), as described in *Materials and Methods*. Fig. 1 displays transmission IR spectra of two sets of samples focused on the spectral windows of the antisymmetrical stretch (ν_3 , *Left*) and bending (ν_2 , *Right*) motions of CO₂. This figure also shows how the profiles of the corresponding IR bands change with the increasing thickness of the sample, from the thinnest one [2 monolayers (ML), Fig. 1 (*Lower*)] to the thickest one [360 ML, Fig. 1 (*Upper*)]. Whereas for the 2-ML ice, the band frequencies may be affected by interaction with the potassium bromide substrate, for a 13-ML sample, the bands agree with the wavenumber positions commonly reported in the literature for thick ices.

The integrated absorptions of these bands allow us to estimate the column density of the deposits, and hence their thickness (18, 19). The strongest feature, at 2,343 cm⁻¹ (4.27 μ m), is assigned to ν_3 of crystalline CO₂, but the origin of the satellite band at 2,328 cm⁻¹ (4.30 μ m), sometimes referred to as “a low-frequency shoulder” (11) (henceforth, X mode), is still unclear. In previous investigations, it was assigned to perturbed CO₂ structures formed when mixed with other components in the ice, such as water (H₂O) (11, 20), which is usually present in astrophysical dust particles but is seen here in pure CO₂ ice. The intensity ratio between the two peaks is clearly dependent on the thickness of the solid, but with the X mode more prominent at low thicknesses. In Fig. 1 (*Right*), spectral alterations with sample growth consist of an increase in the high-frequency component of the ν_2

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Fig. 1. Transmission spectra of CO₂ ice samples deposited at 8 K for increasing thickness, expressed as monolayer coverage. (Upper) Thicker samples are shown. Spectral regions of ν_3 (Left; stretching mode) and ν_2 (Right; bending mode) are also shown. Dashed lines indicate the position of the main vibrational modes: the fundamental (ν_3) and X modes for the stretching region and the so-called “in-plane” and “out-of-plane” modes for the bending region, which are more precisely characterized in this work. A CO₂ molecule (red balls, O atoms; purple ball, C atom) is schematically represented at Top, where the arrows indicate an asymmetric stretching motion (Left) and a bending motion (Right).

doublet, ν_{2b} , at 660 cm⁻¹ (15.15 μm), with respect to the low-frequency part, ν_{2a} , at 655 cm⁻¹ (15.3 μm). For the thickest ices, the spectrum resembles the well-known double-peaked profile that is characteristic of pure and crystalline CO₂ ice. In our experiments, where CO₂ is the only species in the ice, these observations can be rationalized in terms of a crystallization process without requiring the presence of water or other molecular components that lead to a single-band profile near 655 cm⁻¹. Indeed, Fig. 1 shows that the depositions of a few ice monolayers of pure CO₂ also display a single band at that position. Additional experiments and theoretical models described below support this assumption.

The substrate where the ices are deposited can be warmed up until complete sublimation of the sample occurs at ~85 K. Fig. 2 shows spectral variations taking place on a 10-K deposit during

warm-up at a rate of 1 K·min⁻¹. This slow warming induces crystallization of amorphous structures, which is practically attained for CO₂ at ~30 K because there are no significant spectral variations above that temperature. The spectra show that the changes undergone in the lapse of temperature between 10 K and 30 K resemble those observed along the build-up of the samples described above. Thus, the warm-up of the sample to ~30 K by heating the substrate stimulates an effect similar to the accumulation of successive layers at a lower temperature. This process was studied in great detail by Schulze and Abe (21). Complete crystallization, however, is only achieved by thermal annealing. Without warm-up, even the thickest ice sample deposited, 360 ML, still displays a shoulder at 2,328 cm⁻¹ and an intensity ratio of the bending modes that is indicative of not fully crystalline ice.

Transmission spectroscopy of thin films with a normal incidence to the substrate, as performed in the experiments described above, is sensitive to vibrations taking place in the plane of the substrate or with vector components in that plane. Using the experimental set-up available at the Instituto de Estructura de la Materia (IEM), we have recorded reflection-absorption IR (RAIR) spectra with a 75° incidence angle and radiation polarized in the plane of propagation of the incident radiation (P-polarized RAIR spectra). This technique complements transmission spectroscopy in that it allows observation of vibrations in a normal direction to the substrate or with vector components along that direction (22). Fig. 3 presents P-polarized RAIR spectra of a sample deposited at 14 K with thickness growing between 6 ML and 36 ML. Black dashed lines indicate the position of the ν_3 and X bands in Fig. 3 (Left) and of the ν_{2b} , ν_{2a} pair in Fig. 3 (Right), as in Figs. 1 and 2. A red dashed line in Fig. 3 shows the position of the LO modes associated with ν_3 and ν_2 , as measured in a transmission experiment with a 30° incidence angle of a crystalline CO₂ thin sample (additional details are provided in *Materials and Methods*). Thus, the trend of the spectra in Fig. 3 A and B, where the longitudinal modes sharpen and approach the LO maximum, indicates again that the crystallization process is taking place in the sample during its growth. In addition, it can be seen that whereas ν_3 and ν_{2a} become more distinguishable along the series, the X band is completely missing on these spectra, as is the ν_{2b} component. In consequence, we can conclude that the corresponding modes, X and ν_{2b} , oscillate essentially in a plane parallel to the substrate.

To complement these experiments, we have made computer models of amorphous and crystalline CO₂. Pure crystals are straightforward to simulate using the available geometry from X-ray diffraction (23) measurements. On the contrary, the main difficulty in modeling amorphous CO₂ is to devise a sufficiently amorphous initial structure. Low-temperature crystalline CO₂ has a density of 1.78 g/cm³, but the amorphous ice is more porous, with densities that can change within a range of values (21). Thus, to realize a low-density amorphous model, we took an ensemble of 32 CO₂ molecules initially arranged as a set of eight unit cells of the crystal, enlarged the volume of the cell to a selected size to reduce the density, and subjected the sample to increasing temperature to jolt the molecules away from their crystalline equilibrium structure by means of molecular dynamics (MD) simulations. In this way, we prepared models with densities of 1.0 g/cm³ and 1.3 g/cm³. The strength of the intermolecular forces in the crystal for CO₂ is such that even for these low densities, we had to increase the temperature of the MD reactor to unrealistic values (500 K) before an amorphous, or fully disordered, structure could be reached.

The solids thus designed were treated with the SIESTA method (24–26), a well-known and widely used computational tool specifically designed for solids and repetitive units. The initial structures can be relaxed until a well-defined minimum is found on the potential energy surface, for which the vibrational spectrum can be predicted. The unit cell of CO₂ crystals belongs

Fig. 2. Thermal variation of a 30-ML sample from the deposition temperature at 10 K to complete sublimation at 85 K. Spectra are offset for clarity. The arrow on the right indicates increasing temperature along the experiment.

to the Pa3 space group and contains four molecules arranged at alternate corners of a cubic structure. From the IR-active vibrational modes of the four molecules, crystal modes are generated with different IR activity (27): The doubly degenerate ν_2 vibrations split into three independent modes, two of F_u symmetry and one of E_u symmetry, and ν_3 yields one F_u mode and one A_u mode. Of these, only the F_u vibrations are IR-active in the crystal, and they are usually labeled ν_{2a} , ν_{2b} , and ν_3 , respectively. All these vibrations are predicted in our models. Fig. 4 presents a composite of schematic representations of crystalline and amorphous structures with the corresponding predicted spectra, which appear with a red shift from the experimental measurements of $\sim 50\text{ cm}^{-1}$ and 43 cm^{-1} for the ν_3 and ν_2 regions, respectively, that can be attributed to imperfections in the model.

The aim of these theoretical calculations was not to achieve a perfect match in frequency with the experiment but to develop a joint model for crystalline and amorphous CO₂ that provides explanations for the special characteristics of their IR spectra.

Several aspects of the calculations deserve special mention. First, the IR-inactive A_u component of ν_3 is calculated with a red shift of 14 cm^{-1} from ν_3 , that is, coincident with the red shift of the X band from the observed ν_3 . The symmetry restrictions that force the A_u mode to cancel along the crystal do not apply to the amorphous structures, where this band is consequently allowed. Thus, the unexplained origin of the X band seems clear: It is a pure CO_2 mode that can only be seen in IR spectra when amorphous or disordered structures are present. Furthermore, the fact that the X band near $2,328\text{ cm}^{-1}$ was not detected in IR spectra of dense clouds and circumstellar regions, where the other CO_2 ice bands were observed, indicates that, so far, there is no evidence for the presence of pure and amorphous CO_2 ice in these environments.

Second, when the Cartesian components of the ν_{2a} and ν_{2b} modes are analyzed, their predicted orientation sets ν_{2a} in a tilted direction and sets ν_{2b} within the x - y plane. If we assume that the substrate defines the x - y plane, ν_{2a} would be oblique to the substrate and ν_{2b} would be in-plane, in agreement with the observed activity of these modes in normal incidence transmission and in P-polarized RAIR. Vectors depicting these modes are represented in Fig. 4 (*Top*).

Fig. 4 also shows how features in the spectra of the amorphous models evolve toward those of the crystal as the density is increased: The X band, at a frequency *ca.* 14 cm⁻¹ lower than that of ν_3 , becomes weaker and ν_3 becomes stronger in this sequence, and in the ν_2 region, the ν_{2a} component gains intensity and ν_{2b} starts to form.

This work has implications for the interpretation of ice mantle observations in the mid-IR spectral range. The fact that no band around $4.30\text{ }\mu\text{m}$ ($2,328\text{ cm}^{-1}$) was clearly detected in the ice spectra toward dense clouds and protostars confirms that pure CO_2 ice is formed at temperatures above 25 K . This agrees with recent models of ice mantle evolution in protostellar envelopes, where pure and crystalline CO_2 ice is formed after distillation of CO at $\sim 20\text{--}30\text{ K}$, and perhaps also at higher temperatures, leading to CO_2 inclusions in the water and ice matrix (9, 10). The $\text{CO}_2/\text{H}_2\text{O}$ ice mixture displays a single band around $15.3\text{ }\mu\text{m}$ (655 cm^{-1}) that is extensively used as one of the components to fit the bending modes of CO_2 ice observed (9, 10, 20). Fig. 1 shows

Fig. 3. RAIR spectra of CO₂ samples deposited at 14 K with a growing thickness between 6 and 36 ML. Black dashed lines mark the wavenumber position, in decreasing frequency, of the ν_3 and X modes (A) and of the ν_{2b} and ν_{2a} components (B). Red dashed lines indicate the observed wavenumber for the LO modes in transmission spectra of pure crystals at a 30° incidence (19).

Fig. 4. (Bottom) Theoretical models for crystalline (Left) and amorphous (Right) CO₂ solids; the amorphous solid is obtained from the crystalline solid by MD annealing. (Middle) Calculated spectra of crystalline (black) and amorphous CO₂ with densities of 1.0 g cm⁻³ and 1.3 g cm⁻³ (in red and green, respectively). (Top) Predicted orientation of the ν_{2a} and ν_{2b} components of the bending. The ν_{2b} component is practically contained in the x-y plane.

that a single band at a similar position is also obtained by depositing a few ice monolayers (less than ~50 ML) of pure CO₂ if the ice temperature does not exceed ~25 K. However, if we accept that the CO₂ observed in the ice mantles has experienced temperatures above 25 K, as the absence of a 4.30- μ m (2,328-cm⁻¹) band indicates and current astrophysical models suggest (9, 10), the detection of the 15.3- μ m (655-cm⁻¹) component must require mixing of CO₂ with species like H₂O in the polar ice phase. On the other hand, the detection of the two bending modes at 15.15 μ m and 15.3 μ m in other lines of sight, for ice mantles in which CO₂ is mixed with H₂O and other species, implies that segregation temperatures above 25 K were reached, as proposed by Gerakines et al. (20).

In summary, our detailed study of pure and solid CO₂ supports the current scenario for the formation of pure CO₂ ice by two processes. These processes consist of CO₂ segregation out of a CO₂-H₂O mixture at high temperature (50–80 K), on the one hand, and CO evaporation from a CO₂-CO mixture, leaving pure CO₂ behind, at a lower temperature (20–30 K), on the other hand (9, 10, 20, 28). Accordingly, pure CO₂ ice present in ice mantles has experienced a temperature of at least 20–30 K. We show that

at around 25 K, the band near 4.30 μ m (2,328 cm⁻¹) tracing pure and highly amorphous CO₂ ice disappears. As a consequence, pure CO₂ ice in space cannot be completely amorphous. Further evidence is provided by the absence of this band in the published spectra of CO₂ ice observed toward dense clouds and protostars. An example is shown in Fig. 5, where our laboratory spectra are compared with those of Elias 16 (29), a field star probing the ice in a dark cloud.

Materials and Methods

ISAC at the CAB. A set of experiments was performed using the ISAC of the CAB, as described in detail by Muñoz Caro et al. (17). The optimum vacuum conditions, base pressure in the range of 10⁻¹¹ mbar, and use of a needle valve allowed the deposition of CO₂ ice at a very low rate. The column density of the deposited ice was calculated according to the formula

$$N = \frac{\int_{\text{band}} \tau_{\nu} d\nu}{A}, \quad [1]$$

where N is the column density (in square centimeters), τ_{ν} is the optical depth of the band, $d\nu$ is the wavenumber differential (in cm⁻¹), and A is the band strength (in cm-molecule⁻¹). The integrated absorbance is equal to $0.43 \times \tau$,

deposited at 14 K recorded with normal (black trace) and oblique (red) incidence light. The sample displays some crystalline character due to the layer accumulation even at this low temperature, as evidenced by the splitting of the ν_2 modes. The LO modes appear blue-shifted with respect to the transverse modes. Fig. 6 (Lower) presents calculated spectra of a $1.3\text{-g}\cdot\text{cm}^{-3}$ amorphous model, showing the important intensity transfer that takes place when the appropriate electrostatic dipole–dipole interactions are taken into account (28). It can be seen that our calculations predict a LO–TO displacement in good agreement with the observed values for amorphous CO_2 .

Theoretical Method. The specific method and parameters used for our SIESTA calculations follow those used in a previous study by our group (22). Specifically, we have performed density functional theory calculations using Perdew–Burke–Ernzerhof exchange–correlation functionals (37) of the generalized gradient approximation. The basis set for the valence electrons was double-Z polarized (38). The force tolerance parameter was set to $0.5\text{ meV}\cdot\text{\AA}^{-1}$ for the amorphous systems and to $0.05\text{ meV}\cdot\text{\AA}^{-1}$ for the crystalline species. The stress tolerance was set 0.1 GPa , a fairly large value but reasonable for our fixed-cell calculations. Born effective charges for the prediction of absorption intensities have been evaluated by numerical derivation of the macroscopic polarization, with a displacement step of 0.02 Bohr , the same value as in

the force constants calculation. The electronic contribution to the polarization was calculated using the Berry phase formalism (39), by discrete integration over the points of a grid with dimensions of $5 \times 2 \times 2$.

Initial structures for the amorphous systems were obtained by MD annealing simulations of a 32-molecule ensemble, with a target temperature of 500 K , at 1-fs steps, and with the same parameters for the SIESTA method as described above, where appropriate. At the end of the run, the geometrical configuration of the system was taken as the starting point for relaxation and prediction of the spectra. A graphical representation of the crystal and of the $1.0\text{-g}\cdot\text{cm}^{-3}$ amorphous structure is shown in Fig. 4, together with the IR predicted spectra. Densities of $1.0\text{ g}\cdot\text{cm}^{-3}$ and $1.3\text{ g}\cdot\text{cm}^{-3}$ of the amorphous systems correspond to original cubic unit cells with side lengths of $6.630\text{ \AA}$ and $6.079\text{ \AA}$, respectively ($5.624\text{ \AA}$ for the crystal).

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