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LETTER

Letter to the Editor

Ice segregation toward massive protostars

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Abstract. Recent ISO results allow new insights into the evolution of interstellar ices in the vicinity of massive protostars. The presence of CO_2 ice has recently been confirmed with the SWS (Short Wavelength Spectrometer) on-board ISO as a dominant ice component of interstellar grain mantles. The bending mode of CO_2 ice, currently observed toward many massive protostars, shows a particular triple-peak structure. We report on recent laboratory results which identify the CO_2 bending mode feature in dense clouds with molecular complexes formed between CO_2 and CH_3OH ice, which become spectroscopically discernible during the ice segregation process. The comparison of laboratory data and the ISO spectrum of RAFGL7009S indicates the presence of an ice layer with a composition of CO_2, CH_3OH and H_2O in equal proportions. This paper shows evidence for ice segregation and thermal processing in the line-of-sight toward massive protostars.

Key words: ISM: molecules – dust – infrared: interstellar: lines – ISM: individual: RAFGL7009S

1. Introduction

Molecular clouds are composed of interstellar gas and a small amount of interstellar dust. They contain different environments, such as dense cores, which are characterized by very low temperatures (10–30 K) and high densities (10^{4-8} hydrogen atoms cm^{-3}). Such dense cores are the site of star formation and the regions where interstellar ices form. Astronomical observations indicate the existence of different types of ices in quiescent and protostellar environments and toward field stars (Tielens & Whittet 1997). Hydrogen-rich ices (polar ices), dominated by H_2O ice, are formed when H is abundant in the interstellar gas. Hydrogen-poor ice (apolar ices), dominated by CO, are directly accreted from the gas phase in regions where CO is abundant, but H and O are depleted in the interstellar gas.

The ISO-SWS instrument offering a large wavelength coverage and a resolution well adapted to the solid phase is about to change our knowledge of the physical-chemical properties of ices in space. The discovery of many new ice features was reported and the comparison with dedicated laboratory experiments allowed to determine more accurate abundances of major ice components (Ehrenfreund et al. 1997a). ISO has confirmed the ubiquity of solid CO_2 detected by IRAS-LRS in the spectra of 3 protostars (d'Hendecourt & Jourdain de Muizon 1989). A relative high abundance of solid CO_2, namely 15–20% compared to H_2O ice has been recently reported (de Graauw et al. 1996, d'Hendecourt et al. 1996, Guertler et al. 1996). The abundance of CH_3OH has been a debated subject for several years (Allamandola et al. 1992, Skinner et al. 1992). Recent ground-based observations of CH_3OH bands in the NIR (near-infrared) toward RAFGL7009S seem to confirm high methanol abundances toward some massive protostars (Dartois et al. 1998a). NH_3 has recently been detected by ground-based observations with an estimated abundance of $\sim 10\%$ relative to water ice (Lacy et al. 1998). Traces of other species on the few% level for CH_4, HCOOH and possibly H_2CO have been reported from ISO spectra toward selected sources (see Ehrenfreund et al. 1997a and Schutte 1998 for a review).

In this letter, we present laboratory data that allow the exact reproduction of the CO_2 bending mode observed toward RAFGL7009S. The results indicate that thermal processing of ices in the line of sight toward protostellar objects is an efficient process.

2. Experimental

Interstellar ices are simulated using low temperature and vacuum techniques in combination with infrared spectroscopy. Ices are condensed as pure gases or gas mixtures onto the surface of a CsI window in a high vacuum chamber and cooled by a closed-cycle He refrigerator to 10 K. Infrared transmission spectra were obtained with a BioRad FTS 40A (Leiden) and a Brucker FTS IFS 66v (Paris) spectrometer at a resolution of 1 cm^{-1}.

3. Results

3.1. Laboratory spectroscopy

Laboratory data show that solid CO_2 invokes particular interactions with other polar and apolar molecules, which result in strong spectroscopic diversity (Reed et al. 1986, Sandford &

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Allamandola 1990, Ehrenfreund et al. 1996, 1997b). Therefore the profiles of major ice species can be used to determine if and how those components are mixed together.

Fig. 1 shows the CO_2 bend during a warm-up sequence of a H_2O-CH_3OH-CO_2 mixture, characterized by a broad asymmetric profile at 10 K. During heating this profile converts in a multipeak structure. A quite symmetric double peak is observed at 15.15 μm (660 cm^{-1}) and 15.25 μm (655 cm^{-1}) as well as a shoulder at 15.4 μm (649 cm^{-1}), which disappears when the temperature is increasing. The pronounced double peak at 15.2 μm is observed exclusively for pure and annealed CO_2, the vibration being doubly degenerate (Ehrenfreund et al. 1997b).

A survey in the laboratory, using different molecules, allowed us to identify the shoulder at 15.4 μm with specific complexes formed between CO_2 and another polar molecule. In order to reveal the nature of the particular complex several molecules of astronomical importance, such as CH_3OH, C_2H_5OH, HCOOH or NH_3 have been tested. The band at 15.4 μm is formed due to an acid-base interaction between the C atom of CO_2 and the oxygen atom of a specific polar molecule, which in interstellar space is likely CH_3OH. The CO_2 molecule is acting as a Lewis acid and has the ability to form a very stable complex. A similar complex formation is also observed for CO_2-C_2H_5OH mixtures (see Fig. 2). A detailed analysis of the band position and width let us conclude that the abundance of H_2O must have approximately the same proportion as CH_3OH and CO_2 to fit the astrophysical data. When polar molecules, such as H_2O, NH_3 and HCOOH are dominant in the ice, their presence inhibits the complex formation with CO_2, because they are involved in efficient H-bonding (e.g. Ehrenfreund et al. 1997b, see Fig. 11). When water ice is more abundant than CH_3OH and CO_2 the shoulder at 15.4 μm is not present (see Fig. 2, upper panel). The nature of this complex is furthermore constrained by the fact that only mixtures close to a 1:1 ratio provide a good fit to astronomical spectra. For a detailed description of the Lewis complex involving CO_2 and the spectroscopic properties of CO_2/CH_3OH mixtures the reader is referred to more extended papers (Dartois et al. 1999, Ehrenfreund et al. 1999).

3.2. Comparison of laboratory and astronomical data

RAFGL7009S is a massive young stellar object (YSO) located apart from the galactic plane. Infrared observations with ISO already showed that it is an extraordinary source to study solids as well as gas phase species, as it is deeply embedded (d'Hendecourt et al. 1996, Dartois et al. 1998b). Among the species detected in the solid phase is CO_2, with a line of sight ratio relative to H_2O of ~ 20%.

Fig. 2 shows the bending mode of CO_2 toward the massive protostar RAFGL7009S, which is characterized by a triple-peak structure. This characteristic multi-peak feature is currently observed with ISO toward ~ 20 protostars (Gerakines et al. 1999, Boogert et al. 1999). This particular mode shows two sharp peaks at 15.15 and 15.25 μm and a broad wing at 15.4 μm. Comparison with laboratory data are made in two steps. The first

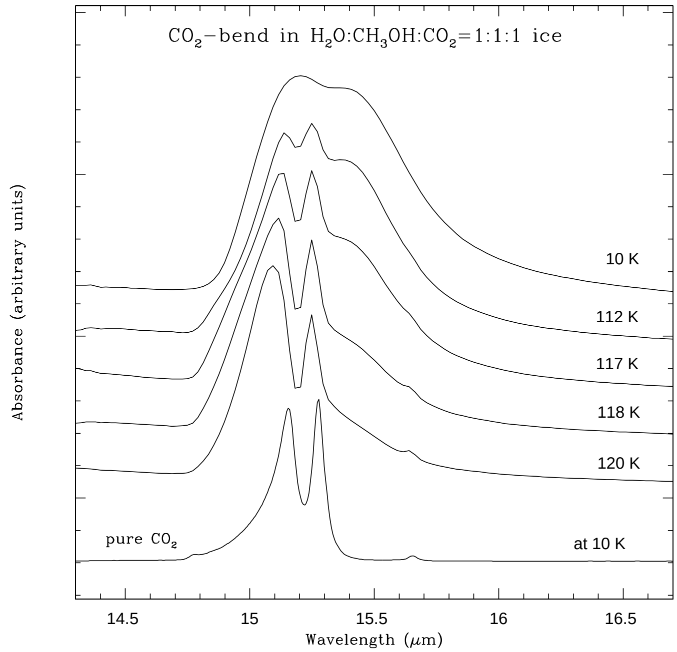

Fig. 1. The CO_2 bending mode at 15.2 μm (658 cm^{-1}) during a warm-up sequence of a H_2O-CH_3OH-CO_2 mixture, characterized by a broad asymmetric profile at low temperatures. During heating this profile converts in a multipeak structure, which is identical to the observations toward several massive protostars.

trace above ISO data in Fig. 2 represents the laboratory spectrum of CO_2-C_2H_5OH=1:1 ice, annealed to ~ 90 K. Ethanol is likely not responsible for the observed multipeak structure of the CO_2 bending mode of RAFGL7009S, because of the absence of the main other vibrational modes in its spectrum. It is used to illustrate the nature of the complex between ethanol and CO_2. Just above we display the same spectrum with the addition of the CO_2 gas phase absorption responsible for the sharp Q branch at 14.97 μm (Dartois et al. 1998b). On the middle panel the same comparison has been performed with a H_2O-CH_3OH-CO_2=1:1:1 mixture. Methanol is a more logical candidate to account for the structure of the CO_2 bending mode, since it is observed toward many protostellar targets (e.g. Allamandola et al. 1992, Dartois et al. 1998a). If the amount of water is slowly increased, the bending mode profile changes, shifts and the 15.4 μm feature progressively vanishes. Note that the results also show that intermolecular interactions completely dominate the behavior of the line profiles and particle shape/size effects in heated ices are negligible, at least in this class of objects. The present laboratory results provide strong evidence that in dense clouds around massive protostars thermal processing dominates the evolution of interstellar ices.

4. Discussion

Having established that the 15.2 μm CO_2 bending mode exibits a substructure associated with the formation of molecular complexes, it is important to confirm that these laboratory results are compatible with the interstellar abundances of the major ice

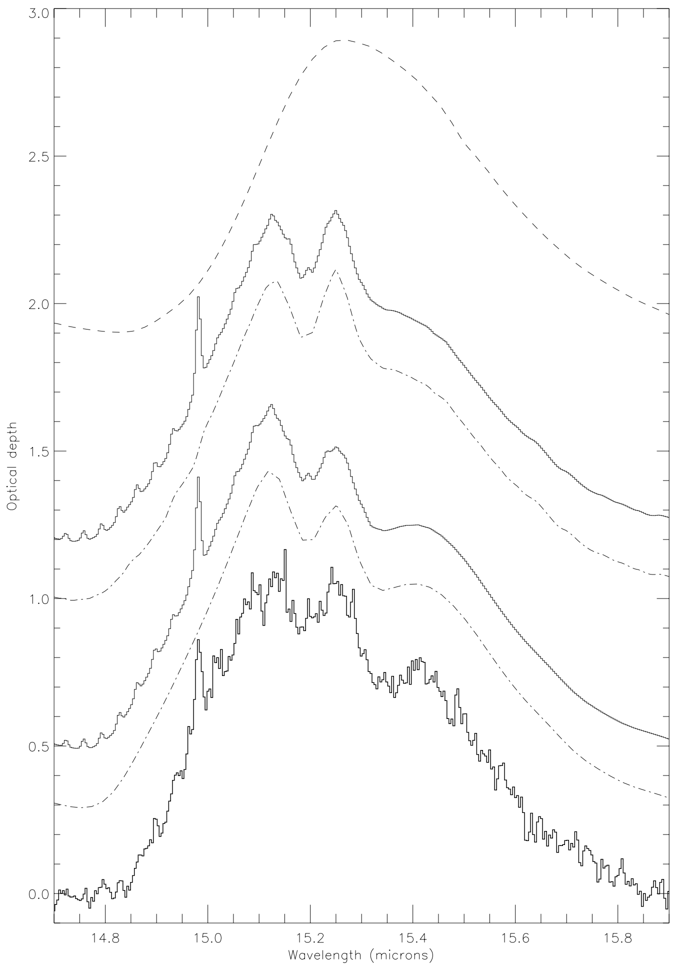

Fig. 2. The ISO-SWS06 spectrum of the CO_2 bending mode at 15.2 μm toward the massive protostar RAFGL7009S is compared with: **lower panel**: a laboratory fit of a CO_2-C_2H_5OH=1:1 ice mixture heated to 90 K (*dashed line*), and a spectrum where the CO_2 gas phase contribution was added (*solid line*); **middle panel**: a laboratory fit of an ice mixture containing equal amounts of H_2O, CH_3OH and CO_2 at 105 K (*dashed line*) and including the CO_2 gas phase contribution (*solid line*); **upper panel**: a spectrum of a polar ice mixture H_2O-CH_3OH-CO_2=10:1:2 at 105 K is displayed as comparison. Please note that the above indicated laboratory temperatures correspond to roughly 50–60 K in dense interstellar clouds. Detailed explanation is provided in the text.

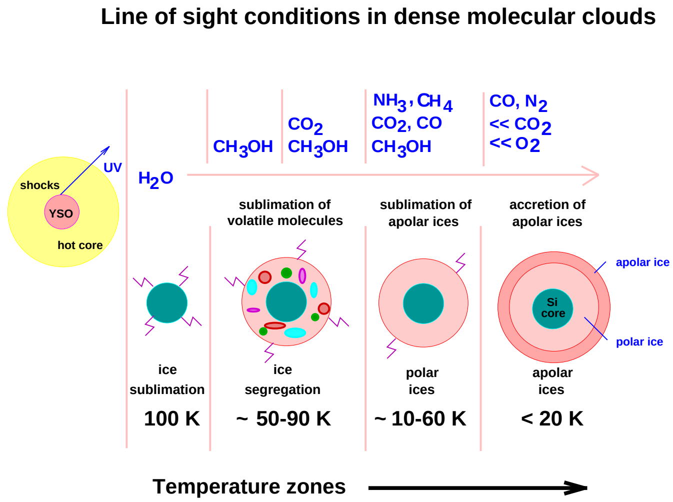

Fig. 3. A schematic drawing of the line-of-sight conditions toward massive protostars. Details are explained in the text.

species involved. Current estimates toward several protostellar sources indicate an abundance ratio of H_2O-CH_3OH-CO_2 $\sim$ 10:1:2 (see Fig. 2, upper panel and Ehrenfreund et al. 1997a). The strong 9.6 μm CO stretch of CH_3OH, could not be measured in the ISO spectrum of RAFGL7009S, because it is embedded in the heavily saturated silicate band. However, recent UKIRT observations of both, the fundamental and combination modes of CH_3OH in the 3–4 μm region indicate a very high abundance of CH_3OH of $\sim$30% relative to H_2O toward this source (Dartois et al. 1998a), which suggests a ratio of H_2O-CH_3OH-CO_2 $\sim$10:3:2 toward RAFGL7009S. Therefore most of the $\sim$20% CO_2 measured toward RAFGL7009S could be mixed with CH_3OH and the remaining CH_3OH may be present in pure form or mixed with H_2O ice. It is evident from Fig. 2 (upper panel) that CO_2 embedded in a water-rich (polar) mixture cannot be responsible for the bending mode structure, neither at low nor high temperature, showing no substructure and an extended red wing. It can however not be excluded that some polar CO_2 could be present and hidden in the large bending mode feature (Gerakines et al. 1999, Boogert et al. 1999).

Fig. 3 displays a schematic drawing of the evolution of interstellar ices composed of a silicate core and an ice mantle in the environment of massive protostars (see also van Dishoeck & Blake 1998). Only the major ice species have been considered in this scheme.

Many recent laboratory results may be used to test the scenario shown in Fig. 3. Polar ices are dominated by H_2O, and contain also some CO, CH_3OH, CO_2, CH_4, NH_3 and other minor species. From band profile studies we can determine that most of the NH_3 and CH_4 but only minor parts of CH_3OH and CO_2 are embedded in water-rich (polar) ice mixtures (Ehrenfreund et al. 1997a, Schutte 1998). Far from the protostar in colder (below 20 K) and denser regions or in "clumps", where CO is abundant in the interstellar gas, apolar ice mantles, dominated by CO, N_2 and some O_2 may accrete as an additional grain mantle layer. The narrow band width of many apolar CO features indicates only negligible admixtures of other species, such as CO_2 (Ehrenfreund et al. 1997b). The temperature rise in the vicinity of protostars is responsible for the evolution of interstellar ice mantles. All pure and trapped ices sublimate at specific temperatures. Above $\sim$50 K the major ice species H_2O, CH_3OH and CO_2 dominate the interstellar ice spectrum and show in comparison with laboratory data that ice layers rearrange, and that complexes between CO_2 and CH_3OH become spectroscopically visible. The multipeak structure of the CO_2 bending mode is only observed in ice mixtures containing CH_3OH (or C_2H_5OH) and heated to temperatures equivalent to $\sim$60 K in interstellar space. Above 80 K, CH_3OH seperates from H_2O, which is consistent with the observations of CH_3OH-

dominated ice layers (Skinner et al. 1992, Dartois et al. 1998a). Above $\sim$90–100 K all major ice species sublimate.

From the presented results we can conclude that an initial ice layer of CO_2, CH_3OH and H_2O in roughly equal abundances must be formed on the grain surface and thereafter be exposed to thermal processing. The efficient production of CO_2 by UV photolysis is well demonstrated in the laboratory (e.g. Ehrenfreund et al. 1997b). Impacts of cosmic rays can also form CO_2 from simple ices and can provide a reasonable fit to the CO_2 bending mode (Strazzulla et al. 1998). The challenging question remains concerning the relative roles of UV and cosmic ray energetic processing or grain surface reactions in the formation of abundant ice species such as CO_2 and CH_3OH.

5. Conclusion

The main results presented here show that the triple peak structure of the 15.2 μm bending mode of solid CO_2, observed with ISO in the SWS spectra of RAFGL7009S, as well as in other protostars, can be satisfactorily duplicated by laboratory experiments involving heated mixtures of H_2O, CH_3OH and CO_2 ices.

The pronounced triple peak structure is explained in terms of the evolution of molecular complexes between a polar molecule (such as CH_3OH) and CO_2 at relatively high temperature ($\sim$50–60 K) in astronomical environments. All astronomical relevant molecules, possibly abundant in grain mantles, have been tested, some of them can give rise to this particular feature. From the abundance criteria, CH_3OH is by far the best candidate. The excellent fit implies that probably all of the observed CO_2 may be heated and involved in CH_3OH-CO_2 complexes, stabilized by H_2O. It can not be excluded that some CO_2, mixed with H_2O ice, may be hidden in the bulk of the same band. If CH_3OH is more abundant than CO_2, as estimated for RAFGL7009S, the remaining amount of CH_3OH may be present in pure form or mixed together with H_2O ice. Finally, we wish to emphasize the excellent quality of the proposed fit, which strongly reinforces the validity of the laboratory approach in the interpretation of ISO data. In this object, at 15 μm, in the bending mode of CO_2 ice, line shifts and shapes can be entirely described by physico-chemical interactions.

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