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A laboratory database of solid CO and CO_2 for ISO *

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Abstract. We present laboratory measured infrared spectra of mixtures containing CO and CO_2 at low temperatures. The profiles and peak position of the absorption features due to these species are very sensitive to molecular environment, temperature, irradiation history and particle shape. Illustrative examples of these variations are briefly discussed.

We have compiled datafiles containing the laboratory spectra, derived optical constants, as well as extinction efficiency calculations for small grains. These files can be retrieved from the WWW in various formats after November 1st, 1996, under http://www.strw.leidenuniv.nl/∼ehrenfreund/isodb. Together with astronomical spectra taken by the ISO satellite these laboratory data will be valuable for the determination of the grain mantle composition and grain evolution in dense clouds.

Key words: ISM: molecules - dust - Infrared: interstellar: lines

1. Introduction

Interstellar dust plays an important role in physical and chemical processes in the interstellar medium. Different dust populations are found in circumstellar envelopes, the diffuse and dense interstellar medium (see Dorschner & Henning 1995 for a review). Within dense clouds grains accrete an ice mantle, consisting of simple molecules such as H_2O, CO, CH_3OH, O_2 (d'Hendecourt et al. 1986). Energetic UV processing of icy grain mantles creates new molecules and radicals which are potential targets for astronomical observations. The comparison of laboratory spectra of astrophysically relevant ice mixtures with interstellar observations have led to the detection of several interstellar solid state molecules and allows to study the gas-grain interactions in interstellar clouds (see review by Whittet 1993).

Water and CO ice are the most abundant molecules in grain mantles as studied by ground based observations (Smith et al. 1991, Chiar et al. 1995). CO_2 has been detected by d'Hendecourt & Jourdain de Muizon (1989) through its bending mode at 15.2 μm in IRAS-LRS spectra. ISO-SWS observations of the 4.27 μm and 15.2 μm bands show that solid CO_2 is ubiquitous in molecular clouds (de Graauw et al. 1996, this volume). Theoretical models and current observations propose the presence of distinct layers on grain mantles and the existence of polar and apolar ices (Sandford et al. 1988, Tielens et al. 1991). The solid CO band of interstellar ice mixtures shows a two-component structure at 2140 cm^{-1}. In comparison with laboratory data it has been deduced that a narrow CO band orginates in apolar ices (CO, CO_2, O_2, N_2), whereas a broad component is attributed to CO in polar ices, dominated by H_2O ice. Due to their volatility apolar ices are observed far away from luminous sources, whereas polar ices are also present close to protostars. The existence of separate individual grain mantle components or perhaps "onion-like" structures on grains has been suggested by observations of solid CO and provide strong constraints for the evolution and life cycle of grains in interstellar clouds (Tielens et al. 1991).

The infrared spectral signature of CO and CO_2 have been previously studied in the laboratory (Sandford et al. 1988, Sandford & Allamandola 1990, Palumbo & Strazulla 1993). We present here a summary of 80 different apolar mixtures and standard polar mixtures measured at temperatures of 10 K, 30 K and 80 K. Furthermore, we have calculated the optical constants and performed particle shape calculations. The presented results are a part of an extensive laboratory program at the Leiden Observatory dedicated to the solid state database for ISO. Besides CO and CO_2, this database also contains spectroscopic studies of CH_4, H_2CO, CH_3OH, SO_2, as well as UV photolysed ices.

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2. Experimental

Ices were condensed as pure gas or gas mixture in a high vacuum chamber on the surface of a CsI window, cooled by a closed cycle He refrigerator to 10 K. Infrared transmission spectra were obtained with a BioRad FTS 40A spectrometer at a resolution of 1 cm^{-1}. Gases and gas mixtures have been prepared in a glass vacuum manifold. The purity of the used gases CO, CO_2, N_2 and O_2 was 99.9997 % (Messer Griesheim). The deposition rate and sample thickness growth rate were about 10^{15} molec cm^{-2} s^{-1} and 1 μm hr^{-1}, respectively. Sample thickness of 0.05 to approximately 0.5 μm have been estimated. A detailed description of the experimental setup has been given by Gerakines et al. (1995).

3. Results

3.1. Laboratory spectroscopy

The variations in peak position, FWHM and profile structure are the result of a complex interplay of the interaction between the molecules present in the ice. This includes dispersive, electrostatic, induced and repulsive interactions (Barnes 1980). Profile variations are also observed during warm up of the ices and after UV irradiation. Broadening of features can reflect these molecular interactions as well as the presence of a distribution of trapping sites. The nature of interaction (repulsive or attractive) determines the band shift as compared to the gas phase.

The Q branch of CO, inactive in the gas phase, occurs at 2143.3 cm^{-1}. Gas phase CO_2 peaks at 2349.1 cm^{-1} for the stretching mode and at 667.4 cm^{-1} for the bending mode. The fundamental transitions of the infrared inactive molecules O_2 and N_2 fall at 1551 cm^{-1} and 2335 cm^{-1}, respectively. These modes become weakly infrared active due to the interaction of the surrounding molecules in the solid state (Ehrenfreund et al. 1992). Astrophysically, we expect that apolar ices will be dominated by CO, O_2, N_2 and CO_2, while polar ices are likely H_2O and/or CH_3OH-rich. We have concentrated in our studies on the interactions of the 4 above mentioned molecules in ice mixtures of binary and multicomponent mixtures in order to constrain the role of apolar ices. The results are presented in detail by Ehrenfreund et al. (1996).

3.2. Particle shape calculations

Interaction of an electromagnetic radiation field with the molecules in small grains can change the absorption profile and peak position. It induces an electric charge near the surface of the grain, and therefore the oscillators in the grain are subjected to applied and induced electric field components. The strength of the induced component depends on the polarizability of the grain, which in turn depends on the grainshape and the dielectric or optical constants of the ice (Bohren & Huffman 1983). The optical constants of all our spectra have been calculated using the Kramers-Kronig analysis as described in Hudgins et al. (1993). A more detailed description of the determination of the optical constants and subsequent particle shape calculations for our ice mixtures can be found in Ehrenfreund et al. (1996).

3.3. CO and CO_2

Representative spectra of the CO and CO_2 stretching mode are shown in Figures 1 and 2. The 2340 cm^{-1} symmetric stretching mode of pure CO_2 is rather unique, showing a large FWHM and wings on the high and low frequency side at 10 K (see Fig. 2). The precise profile of this band is very sensitive to the molecular environment, reflecting the importance of multiple trapping sites and the ease with which CO_2 forms complexes with a variety of species. The CO_2 bending fundamental falls near 650 cm^{-1} (15.2 μm). This vibration is doubly degenerate and the band splits when the axial symmetry of the molecule is broken and pure CO_2 shows a clear double peaked structure in the bending mode. A less pronounced double structure (where the high frequency peak is seen as a shoulder) appears in $CO/O_2/CO_2$ mixtures, as shown in Fig.3. The CO_2 bend is especially sensitive to the ice composition. The presence of other species in a CO_2 matrix leads to a general blending of the two separate peaks as seen in CO/CO_2 and many multicomponent mixtures. In most polar mixtures only one peak remains. The presence of CO_2 also influences the detailed profile of bands by other species. This is particularly pronounced for the CO fundamental (cf. Fig. 1). A strong change in FWHM (3 cm^{-1}) is observed when the concentration of CO_2 in the mixture changes from 21 to 23 % indicating the importance of steric interactions induced by the presence of CO_2.

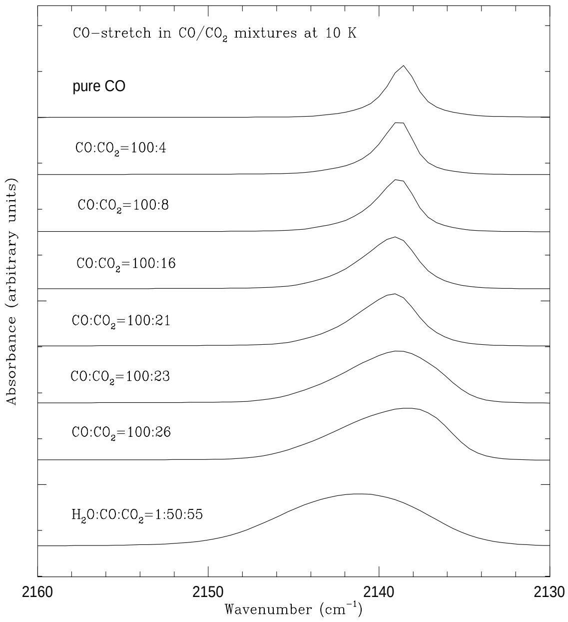

Fig. 1. Infrared absorption spectra of solid CO in CO/CO_2 mixtures. A sharp transition in the CO band width occurs when the amount of CO_2 in the mixture exceeds 22 %. This concentration initiates a strong change in the steric configuration of the ice matrix.

Besides the physical and chemical environment these spectra may also contain information on the chemical history of the ice. In particular, CO_2 is readily formed by UV photolysis of H_2O/CO mixtures. The CO band (at 2136 cm^{-1}), shows a shoulder, centered near 2152 cm^{-1} in all binary ice mixtures in which water is the main component. This band is assigned to CO-H_2O hydrogen bonded complexes in water ice (Jenniskens et al. 1995). Upon irradiation this feature disappears rapidly, because CO_2 is created in a very efficient way from this H_2O-CO complex (Ehrenfreund et al. 1996).

From warm-up experiments we derive that CO, N_2 and O_2 are sublimated around 20 K under astrophysical conditions, pure CO_2 is less volatile (T=56-80 K) and can survive somewhat closer to the star. When CO is embedded in water ice it can diffuse through the H_2O lattice and is sublimed at T=65 K. The evaporation of CO_2 from polar ices occurs between T=85-150 K, depending on the CO_2 concentration. Large amounts of CO_2 mixed with water lead to strong aggregates, complexes and a fragile ice matrix, and CO_2 evaporates around 85 K, similar to pure CO_2 (Sandford & Allamandola 1990).

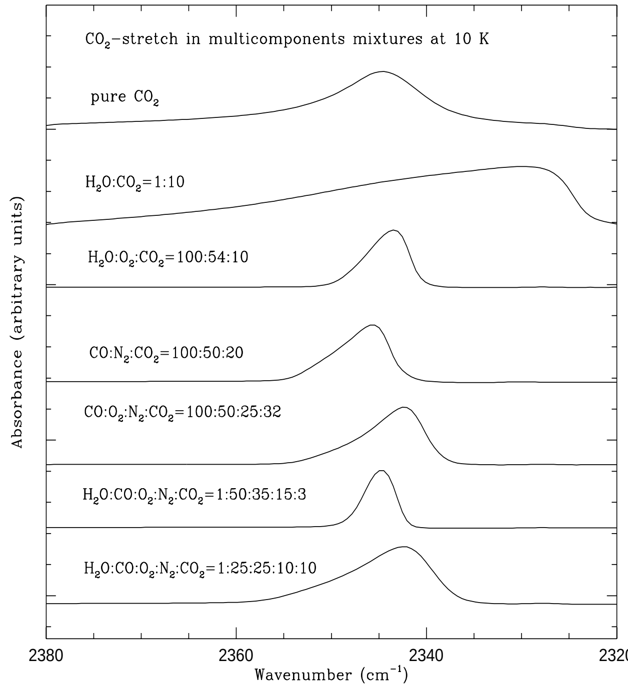

Fig. 2. Infrared absoption spectra of the CO_2 band in multicomponent mixtures. This figure illustrates the strong dependence of the CO_2 stretching mode on the ice composition. When more than a few % of water ice are included in the mixture strong profile changes may occur, as observed for a CO_2:H_2O=10:1.

Large amounts of O and N are apparently missing from the gas phase and might be depleted on interstellar grains. Apolar ices might be a reservoir of O_2 and N_2 in molecular clouds. In principle, solid O_2 and N_2 can be detected by their weakly active fundamental transition in solid phase but those observations are very difficult (Ehrenfreund et al. 1992). More likely the presence of these molecules could be traced by their subtle influence on the absorption features of CO and CO_2. The laboratory experiments presented here form the basis for any such identification. Figs. 2 and 3 show some illustrative examples of the power of this method to probe the infrared inactive component of interstellar ice mantles.

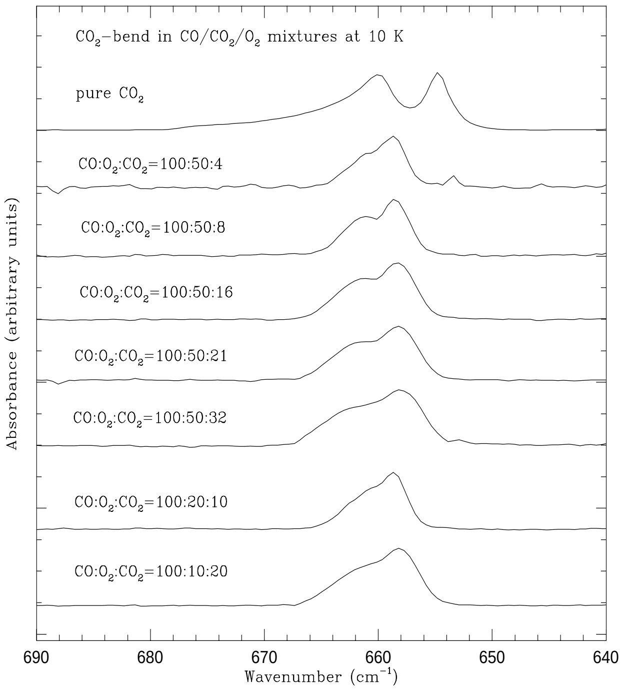

Fig. 3. Infrared absorption spectra of the CO_2 bending mode in CO:O_2:CO_2 mixtures. The double structure is evident for pure CO_2 and can be well distinguished in a CO:O_2:CO_2=100:50:8 mixture. When the concentration of CO_2 in the matrix increases, the formation of complexes leads to a general blending.

Particle size and shape effects can affect the strong absorption features of solid CO and CO_2. We have performed calculations for different particle shapes such as spheres, a continuous distribution of ellipsoids and core/mantle particles with different mantle thickness. An example for a CO_2/H_2O=10:1 ice mixture is given in Fig. 4. The calculations were done in the Rayleigh limit, which is an approximation of Mie theory for particles small compared to the wavelength (Tielens et al. 1991). The upper panel of Fig. 4 shows the real and imaginary part of the dielectric constants of this ice mixture. The lower panel shows the normalized absorption cross section for different particle shapes. The upper spectrum is measured in the laboratory. The sphere shows a peak considerably shifted to the blue, where Re(ϵ) is negative and Im(ϵ) is small (Bohren & Huffman 1983). The next case shows the broad absorption profile for an ensemble of particles where each ellipsoidal shape is equally probable (CDE: 'Continuous Distribution of Ellipsoids'). For the coated grain model we assume a silicate core, and a CO_2/H_2O ice mantle. The core and the mantle have equal volume. Two peaks appear, because surface modes arise at the inner and outer surfaces of the mantle. When the mantle volume is increased with respect to the core, the separation between the peaks decreases till they merge to the one peak for a core-less spherical grain. Finally, the bottom spectrum shows the case of a silicate grain core size distribution (MRN: Mathis, Rumple & Nordsieck 1977), with an ice mantle thickness of 0.01 μm irrespective of the core size. The peaks of the coated grain have merged into one broad profile, because in practice this is an integration over coated grains with a distribution of core/mantle volumes.

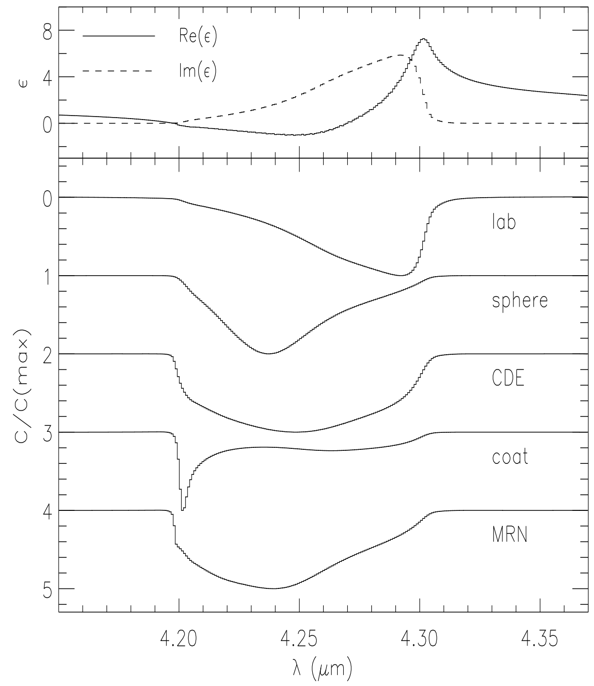

Fig. 4. Infrared absoption spectra of a CO_2/H_2O=10:1 ice mixture in comparison with particle shape calulations. A detailed description is given in 3.3.

We conclude that particle shape and size distributions influence the absorption peak position and width of CO_2 very strongly. We found from our database that particle shape effects have a measurable influence when the CO_2 abundance is more than ∼10%. Note that for CO ices this limit is ∼30% (Tielens et al. 1991), reflecting that the CO_2 stretching mode is much stronger than the CO fundamental, i.e. that Re(ϵ) has a deeper minimum.

4. Discussion

CO and, according to recent ISO observations, also CO_2 are important ices in dense clouds. Peak position and band width of the strong bands of CO and CO_2 indicate not only the polar and apolar character of the ice, but can also give an indication on temperature and radiation history of grains. The study of CO and CO_2 bands provides a powerful tool to determine the grain mantle composition, in particular the presence of solid O_2 and N_2, and the grain evolution in the cycle of interstellar clouds. Initial fits to the ISO data using these laboratory results are presented by de Graauw et al. (1996).

5. Database on the WWW

This Letter is an announcement of a database of solid CO and CO_2 for ISO which can be found on the World Wide Web (WWW). This database contains more than 80 experiments on apolar ices and standard polar mixtures. Additional datafiles exist containing the optical constants n and k. The changes in the profiles are simulated for different particle shapes such as spheres, ellipsoids and core/mantle particles. The link http://www.strw.leidenuniv.nl/∼ehrenfreund/isodb will be active after 1.11.1996 including a help page for explanations. Using this database, observers can try to fit their measured profiles themselves, and assess the influence of any particle shape using the optical constants. A complete paper with the physical interpretation "Infrared spectroscopy of apolar ice analogs" is submitted to A & AS (Ehrenfreund et al. 1996). Please refer to the present paper in the A & A special issue, when using datafiles from the database. We wish you fun and success!

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