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Study of binary ices (CO_2:CH_4, N_2:CH_4, and CO_2:N_2): density and refractive index

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Abstract

In this work we present the results of a series of laboratory experiments performed to obtain the density and refractive index (real part) for binary mixtures of astrophysical interesting ices. Densities of $CO_2 : CH_4$ mixtures obey the expected weighted mean and the other binary mixtures have densities up to 20% lower than expected. Refractive index for all the binary mixtures deviates up to 5% from the theoretical, obtaining higher values than expected for $CO_2 : CH_4$ and lower values than predicted for $CO_2 : N_2$ and $CH_4 : N_2$.

1 Introduction

In Astrophysics, ices are widely studied due to the many scenarios in which they are present. Their abundance varies from one location to another, and the composition and structure of ices respond to their environments [18]. Physical and chemical properties of ices play an important role in the evolution of several scenarios such as: the interstellar medium (ISM), in the denser, cooler regions of molecular clouds [14, 6], and Solar System objects as planets, satellites, even in TNOs [5, 7, 3], and comets [12, 1].

Density is important in the analysis of many results, observational, experimental and theoretical (integrated absorbance, ion irradiation and buoyancy). Up to now, in the literature usually is assumed that the density for all ices is 1 g cm^{-3}, irrespectively of implying pure ices or mixture of them. It is reported [16, 9, 13] that density depends on the molecule and the growing temperature. So, the study of any particular scenario should use, if needed, the density of the pure implied molecules instead of 1 g cm^{-3}. A priori, if the density of certain mixture is needed for calculations, it could be assumed that its density is the arithmetic mean of the density of implied ices. Hereafter theoretical density is defined as the arithmetic weighted mean by the molecular fraction of every molecule. This work shows why it is not necessarily true.

In this paper we present new results on the density and real part of refractive index at 632.8 nm (hereafter refractive index) of binary mixtures.

2 Experimental

The procedure to obtain the refractive index and density is briefly summarized here. A more detailed explanation in some aspects is presented in [16].

We have measured the density and refractive index of binary CH_4, CO_2, N_2 ice mixtures at high vacuum (base pressure 10^{-7} mbar) and low temperature (14 K).

Sample thickness is determined by laser interferometry and a quartz crystal microbalance (QCMB) as a sample holder, is used to calculate the mass of ice accreted per unit area (in g cm^{-2}).

To prepare the sample in the suitable proportion, the procedure is as follows: gases are introduced in the prechamber taking their composition in molar fraction from their partial pressure according to the mixture desired, for example for a mixture 1:1 $CO_2 : N_2$, we have added to the prechamber 45 mbar of CO_2 and 45 mbar of N_2 measured with a capacitive sensor element (CERAVAC CTR 90) which assures a precision higher than 0.2% during deposition. Once prepared, gas flows from the prechamber to the deposit vacuum chamber controlled by a needle valve (Leybold D50968).

To form the ice film, a constant rate of deposition is used, maintaining almost constant the aperture of the valve. Once gases enter the deposition chamber, their composition during film growth is checked through the Quadrupole mass spectrometer (QMS) (Accu-Quad RGA 100) with a resolution of 0.5 amu. The QMS, where the effect of molecules fractionating is taken into account, confirms the relative proportion of the gases entering from the prechamber.

3 Results

We present in this section our experimental data compared to the theoretical ones, as defined in Section 1. For theoretical calculations we take experimental values presented in [16] for pure molecules at 14 K (Table 1).

Table 1: Density (ρ) and refractive index (n) obtained for CH_4, N_2 and CO_2 deposited films at 14 K

Ice	ρ (g cm^{-3})	n
CH_4	0.47	1.30
N_2	0.94	1.21
CO_2	0.98	1.21

Refractive index of binary mixtures is measured by double laser interferometry. Density

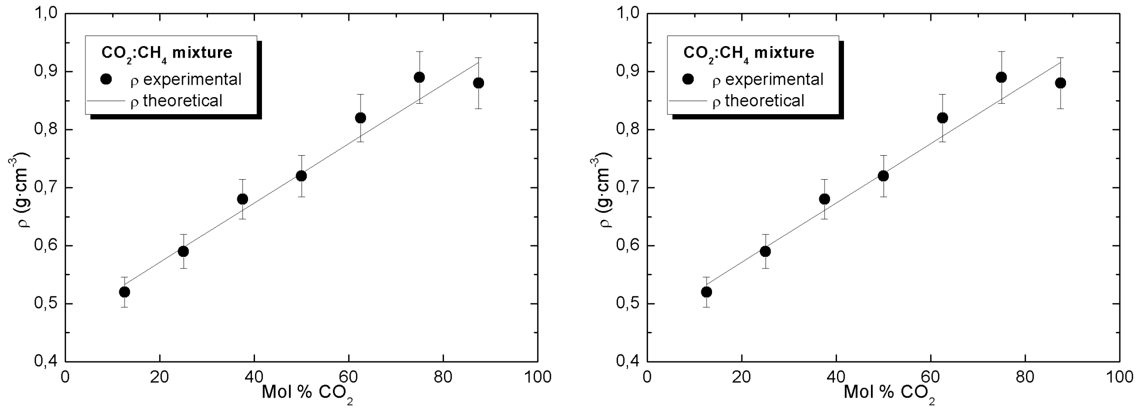

Figure 1: Density (left) and refractive index (right) for CO_2 : CH_4 mixture.

has been calculated as the ratio between QCMB signal and film thickness.

In Figs. 1, 2 and 3 we represent the theoretical results as a straight line and the experimental ones as solid circles. In all of them X axis represents the proportion in percentage of mol fraction of the corresponding denser ice, CO_2 in Figs. 1 and 3, and N_2 in Fig. 2. Y axis shows density in g cm^{-3} in left panels and refractive index in right panels. For a better comparision, left and right panels share the same Y scale.

3.1 CO_2 : CH_4

In Fig. 1 left panel, density of the mixture increases as the CO_2 proportion is higher, fitting the theoretical value despite little deviations observed for the three experimental points at the right side of the plot, but all of them fit the behavior expected taking into account the error bars.

In right panel, refractive index shows deviation from the theoretical ones. Despite the error bars (2.5%), experimental refractive index are slightly over the theoretically calculated value.

3.2 N_2 : CH_4

As previously, Fig. 2 left panel shows that as the mixture is richer in N_2 (the denser pure ice) the density increases. Experimental results, instead of fitting the linear combination of densities, show lower values. Central values are about 20% lower than the theoretical ones (this behavior is relevant even taking into account the error bars). Close to pure ices (10% and 90% in N_2) density values approximate to the theoretical ones.

Right panel shows deviation of about 5% in refractive index respect to theoretical values. In this case the refractive index is lower than the expected one for all the mol fractions, as it occurs for the density.

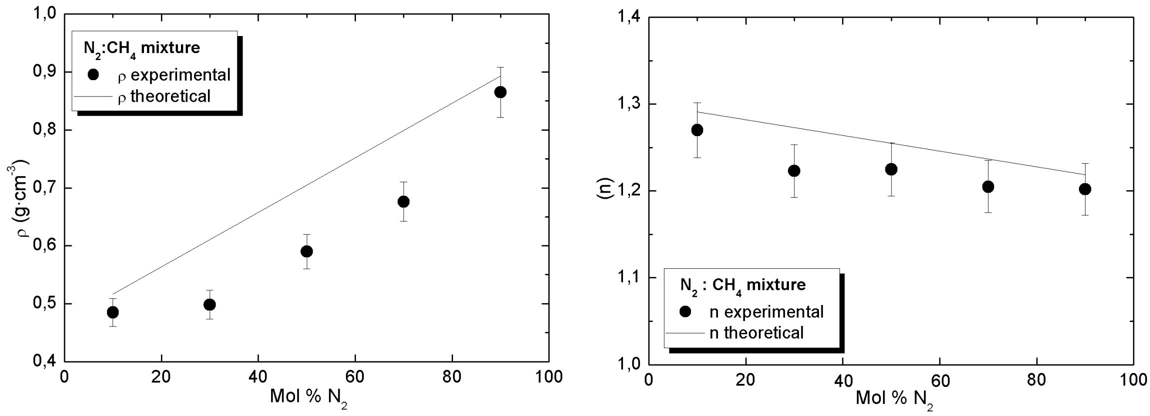

Figure 2: Density (left) and refractive index (right) for $N_2 : CH_4$ mixture.

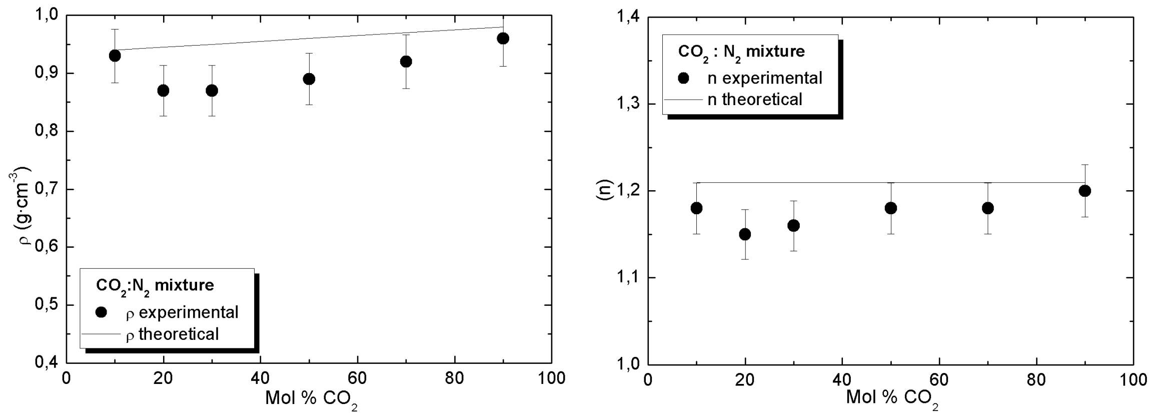

Figure 3: Density (left) and refractive index (right) for $CO_2 : N_2$ mixture.

3.3 $CO_2 : N_2$

CO_2 and N_2 mixture, Fig. 3 (left panel), presents a deviation from the theoretical values of density, specifically a reduction up to 10% of the expected value. As in the previous case, it also shows how the 10% and 90% CO_2 proportion mixtures fit the theoretical values.

Right panel shows deviation of about 5%. In this case the refractive index is lower than the expected one for all the proportions, as it occurs in the case of density.

4 Discussion and conclusions

In this work, density and refractive index of three binary mixtures have been studied, finding in some of them differences from the expected linear behavior. Therefore, a priori, density and refractive index of any binary mixture of ices in astrophysical conditions are not possible to be obtained, in all cases, directly from their mol fraction when their pure ice density and refractive index are known.

The experimental results presented here are discussed taking as starting point the crystal lattice. Crystal structure of these molecules are scarcely studied at 14 K and high vacuum conditions, so it is no possible to confirm whether they are in crystalline or amorphous form. Nevertheless crystalline structure appearing in the literature at low temperature are: FCC (face centered cubic) for CO_2 [4] and CH_4 [17] and HCP (hexagonal close-packed) for N_2 [17]. Considering density (left panels), we distinguish two different graph types. Fig. 1 left panel represents the expected behavior and Figs. 2 3, left panel, a different one. $CH_4 : CO_2$ mixture (Fig. 1), involving pure ices with the same FCC structure, gives a density obeying a theoretical linear behavior. This means that CH_4 molecules accommodate in sites occupied by a molecule of CO_2, maintaining a similar specific volume. On the other hand, when a mixture contains nitrogen, any molecule of CH_4 or CO_2 that comes into the structure of nitrogen (HCP) or vice versa, creates a defect and a corresponding decrease in density because nitrogen itself forms a compact structure perturbed by any different codeposited molecule.

It is known that refractive index depends on the number of particles by volume (density) and the interactions among them. In mixtures, new interactions appear with different type of molecules that are not present when pure ices are formed.

In the experiments involving mixtures $CO_2 : N_2$ and $CH_4 : N_2$ (Figs. 2 and 3), density values decrease respect to the theoretical one and refractive index values diminish as well (less particles in average are present in the optical path, minor the refractive index is). In the case of $CO_2 : CH_4$ mixture (Fig. 1), density fits the theoretical behavior but refractive index shows higher values than expected. In this last experiment the increase (respect to the expected values) can be only explained due to these new interactions appearing among different type of molecules present only in mixtures. This explanation justifies all of our experimental results, i.e. refractive index follows the behavior of the density adding a positive contribution due to interactions among different type of molecules in a mixture.

The work presented here is relevant because the molecules studied are abundant in many astrophysical scenarios. In those, our data would help to obtain values of abundances from the integrated absorbance, where the density is a parameter involved in its calculation.

Another consequence of the results presented here is the buoyancy of mixtures when present in a liquid context. For example the buoyancy of mixtures including N_2 will be greater than expected from their weighted mean as the density could decrease down to 20%. In this way [15] point out the relevance of the buoyancy of ice in the CH_4-N_2 system. Despite the authors center their discussion on Titan, the relevance for other scenarios as Triton, Pluto or Eris is highlighted. In fact, [8], studying Triton surface, encourage additional investigation in a reddish, high albedo material and its possible relationship with the appearance resulting from new CH_4 escaping from Triton deep interior. This could be related to the mentioned buoyancy. The appearance of new fresh methane on the surface of Triton is very interesting and it is connected to the last astrophysical application we expose. Ion irradiation on CH_4 produces dehydrogenation [2], then the presence of pure CH_4 ice on a surface needs a repository of fresh methane that feeds it, because irradiation is relevant for Triton scenario. The presence of high energetic electrons and ions were detected from the measurements with the low-energy charge particle (LECP) instrument on Voyager 2. That ions interact with

Triton, and [10] suggested from that data that Triton is important in controlling the outer regions of the neptunian magnetosphere. Density values influence the penetration depth and damage produced by impinging ions in icy surfaces in the Solar System. A density value lower than expected can be important to explain the absence of CO_2, C_2H_2, C_2H_4 and C_2H_6 on the surface of Pluto and its appearance in the surface of Triton because it is immersed in Neptune's magnetosphere. The relatively low processed surface of Pluto could be similar to the case of the TNO Eris. Irradiation processes seem to have negligible effects on the parameters they studied in this TNO as pointed out by [11].

Acknowledgments

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