

SOLID STATE ASTROPHYSICS AND -CHEMISTRY FOUR QUESTIONS - FOUR ANSWERS

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Abstract. Recent progress in ultra high vacuum surface experiments allows detailed investigations of the physical and chemical parameters governing astronomically relevant solid state processes on icy dust grains. In this proceeding four questions are shortly addressed that are related to the infrared signature, the thermal and photodesorption behavior and the chemical reactivity of interstellar ice analogues.

1 Question 1: How to determine interstellar ice compositions ?

Infrared spectroscopy towards dense molecular clouds and young stellar objects often reveals prominent bands that can be attributed to H₂O ice. It has been a long standing problem in the astronomical community that the observed intensity ratio of the 3 μm stretching mode and the 6 μm bending mode differs as much as a factor two compared to laboratory spectra recorded for pure water ice. Recently, it has been suggested (Knez et al. 2005) that this discrepancy may be due to substantial amounts of other species mixed into the H₂O ice matrix. Two likely pollutants are CO₂ and CO. Incorporation in the ice perturbs the spectroscopic signature of the fundamental vibrations reflection molecular interactions: intensities and intensity ratios change, peak positions shift and band widths are affected. These values are depending on mixing ratio, temperature, morphology and deposition conditions of the ice. I.e. in order to relate an observed astronomical ice spectrum to a specific ice composition it is necessary to determine spectroscopic parameters in systematic dependence of a number of physical parameters. In the last year such systematic spectroscopic searches have been performed for H₂O:CO₂ ices (Öberg et al. 2007a), H₂O:CO ices (Bouwman et al. 2007), HCOOH containing ices, mixed with CH₃OH, HCOOH and H₂O (Bisschop et al 2007a) and NH₃ and CH₃OH containing ices (Bottinelli et al. 2008) using Fourier transform transmission spectroscopy. As an example conclusions for H₂O:CO₂ ices are summarized in a correlation diagram (Fig. 1). The 6:3 μm integrated intensity ratios are shown for values of 0.2, 0.5, 1, 2 and 5 as function of both temperature and mixing ratio.

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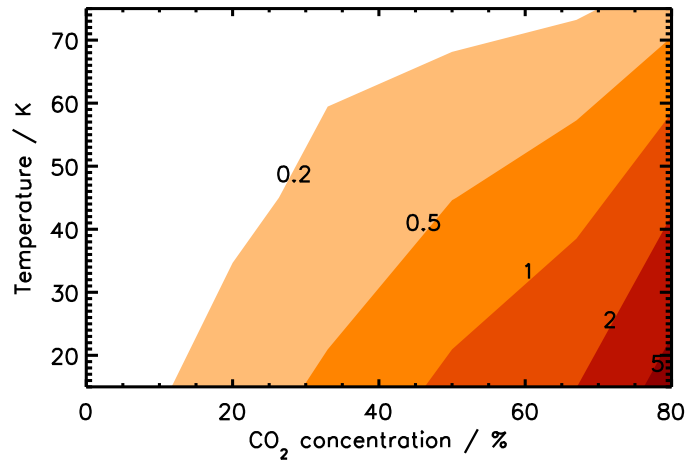


Fig. 1. Correlation diagram showing the 6:3 μm intensity ratio distribution of H_2O ice in dependence of CO_2 concentration and temperature.

In combination with peak position and band width it becomes possible to derive rather specific ice compositions and conditions as recently discussed by Bisschop et al. (2007a) where ISO HCOOH features are reproduced by tertiary laboratory mixtures of formic acid, methanol and water. These spectra together with data available from previous studies are accessible online via the Leiden Ice Database at: <http://www.laboratory-astrophysics.eu>.

2 Question 2: Is molecular oxygen hiding in interstellar ice ?

During the first stages of star formation virtually all species accrete onto grains in dense cold clouds. Later on in the star formation process, grains are warmed to temperatures where molecules can desorb again. Detailed ultra high vacuum experiments applying TPD (temperature programmed desorption) provide accurate information on the involved thermal desorption behavior of astrophysically relevant species and yielding values for the desorption temperature, i.e. binding energy. Typically Polanyi-Wigner type of equations are used to describe the thermal desorption mechanism in terms of an empirical kinetic model.

In the last year special attention has been given in our laboratory to oxygen bearing ices. The reason is that a substantial amount of interstellar oxygen may well freeze out onto grains in the form of molecular oxygen, potentially explaining the very low O_2 -abundances observed in space (Bergin et al. 2000). Recent ODIN/SWAS campaigns (Larson et al. 2007) put upper limits on the O_2 gas abundance in cold dark clouds in the range of 10^{-7} to 10^{-8} with respect to H_2 . This low abundance raises serious questions about the total oxygen budget when compared with the well observed atomic oxygen abundance of $3 \cdot 10^{-4}$ in diffuse clouds (Ehrenfreund & van Dishoeck, 1998). In order to investigate this hypothesis, it is interesting to ask to what extent O_2 differs from CO , since CO is readily observed in the gas phase and in solid form, and how O_2 compares to N_2 that is observed in the gas phase through the detection

of N_2H^+ . For this reason we have studied pure CO, N_2 and O_2 ices as well as layered and mixed CO/ N_2 and CO/ O_2 ices (Öberg et al. 2005, Bisschop et al. 2006, Fuchs et al. 2006, Acharyya et al. 2007).

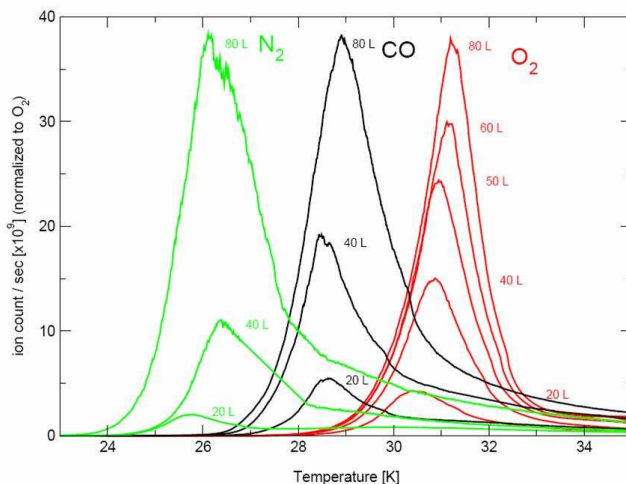


Fig. 2. TPD spectra for pure N_2 , CO and O_2 ices for different layer thicknesses. Clearly the desorption energies of these volatile compounds are very close.

We find that O_2 is less volatile than CO but CO does not co-desorb with O_2 . This is different for CO- N_2 ice for which it is found that N_2 is more volatile than CO and that a significant amount of N_2 co-desorbs with CO. The thermal desorption behavior for pure CO, N_2 and O_2 ices is shown in Figure 2. We conclude (Acharyya et al. 2007) that in cold clouds with $T_d < 18$ K, O_2 can be frozen out onto grains, however, the relative difference in desorption between CO (and N_2) and O_2 is so small that this is unlikely to be the explanation for the missing gaseous O_2 in interstellar clouds that show significant amounts of gaseous CO.

3 Question 3: Why is CO observed in the gas phase well below its accretion temperature ?

Astrochemical models show that in cold and dense interstellar regions all molecules, apart from H_2 , should be frozen out onto dust grains. Submillimeter observations, however, indicate that still substantial amounts of gaseous CO can be identified (Bergin et al. 2002). Similarly, cold CO gas has been detected in the midplanes of protoplanetary disks (Dartois et al. 2003) at temperatures well below the condensation temperature onto grains (see Fig. 2). This means that another desorption mechanism is needed to keep CO molecules in the gas phase and as CO is regarded as a starting point in the formation of more complex molecules (see also Question 4), any information providing additional insights in grain-gas interactions is relevant to describe astrochemical reaction schemes.

Photodesorption has been proposed in the past as a potential desorption pathway in regions with excess UV photons (Dominik et al. 2005) but as desorption rates were

estimated to be negligibly small, of the order of 10^{-5} to 10^{-8} CO molecules / UV photon (e.g. Hartquist & Williams 1990), it generally has been neglected in astrochemical models. New ultra high vacuum experiments in which CO ice is irradiated by UV radiation simulating the interstellar radiation field using a H₂ microwave discharge lamp (roughly 100-200 nm) allow an experimental derivation of the photodesorption rate (Öberg et al. 2007b). In this experiment RAIRS (reflection absorption infrared spectroscopy) is used to monitor the CO absorption signal that is directly proportional to the amount of available CO. Upon irradiation the RAIRS signal linearly decreases with time (see Fig. 3) and as the UV flux is known at the ice surface is known, it is straight forward to derive a value for the photodesorption rate: 3.10^{-3} CO molecules / UV photon.

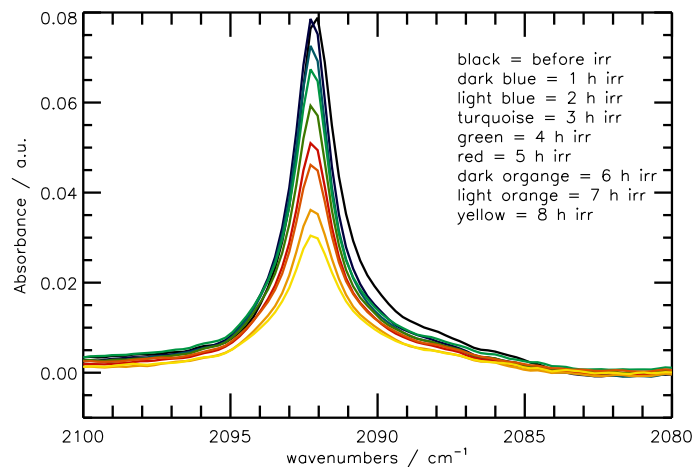


Fig. 3. RAIRS spectra of CO ice as function of time upon UV irradiation using a H₂ MW discharge lamp. The decrease is linear and can be directly related to a photodesorption rate.

This value is substantially higher than assumed so far and incorporation in an astronomical model shows that the value is sufficiently high to explain the observed CO gas phase abundances in dark clouds (Öberg et al. 2007b). Accurate test measurements have been performed to rule out any substrate or UV flux mediated effects. Most strikingly is the fact that an identical experiment for molecular nitrogen ice gives no detectable result. This indicates that the origin of the photodesorption mechanism is most likely related to a rovibrational interaction of CO within the ice matrix upon electronic excitation as N₂ does not possess an allowed electronic transition in the energy range of the H₂ microwave discharge lamp. Currently, work is in progress to monitor the photodesorption of O₂, CO₂ and H₂O as well as the co-desorption of species in mixed ices with CO. For further details the reader is referred to Öberg et al. (2007b).

4 Question 4: Can complex molecules form in interstellar ice analogues ?

Grain surface processes have been proposed over more than two decades as the starting point for the formation of saturated and more complex molecules (see e.g. Tielens

2005). More recent work predicts complete chemical networks on icy grains following atom-bombardment by H-, C-, O- or N-atoms. The very starting point has been the hydrogenation reaction of CO resulting in subsequently formaldehyde and methanol. The proposed mechanism involves H-atom addition in a successive hydrogenation process of CO-ice: $\text{CO} \rightarrow \text{HCO} \rightarrow \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH}$ (Tielens & Whittet, 1997, Charnley et al. 1997). Laboratory studies of H-atom bombardment of CO ice have been performed independently by two groups (Hiraoka et al. 1994, Watanabe et al. 2002). Hiraoka observed only formaldehyde formation, whereas Watanabe also found an effective methanol production. In a series of papers these conflicting results have been discussed (Hiraoka et al. 2002, Watanabe et al. 2003 and 2004) and the existing discrepancy has been explained by different experimental conditions, most noticeable the adopted H-atom flux (Hidaka et al. 2004). An experimental verification, however, has been lacking so far. In order to verify the origin of the conflicting results an additional systematic study has been performed focussing on the physical dependencies that may affect CO ice hydrogenation schemes, in particular: temperature, H-atom flux, layer thickness and ice morphology. The results of this study are summarized in Fuchs et al. (2007). The major conclusions are addressed here shortly:

- Both the formation of H_2CO and CH_3OH are readily observed in CO-ice upon H-atom bombardment using RAIRS and TPD as detection techniques.
- The previously observed discrepancy is indeed very likely due to the different H-atom fluxes used.
- The functional surface temperature dependence of the reaction rates shows a maximum for both H_2CO and CH_3OH around 13-15 K.
- For ices thicker than 10 ML no layer thickness dependent reaction rates are found.

A detailed characterization of solid state astrochemical processes like the hydrogenation of CO-ice is of importance to understand how more complex molecules may be formed in space. The initial reaction schemes introduced by Tielens, Hagen and Charnley (Tielens & Hagen 1982, Tielens & Charnley 1997) have become in reach of experimental approaches, also beyond hydrogenation reactions of CO. Just very recently the formation of ethanol in interstellar ice was demonstrated upon H-atom bombardment of solid acetaldehyde (Bisschop et al. 2007b). Hydrogenation studies of CO_2 and HCOOH are reported there as well. It is clear that with growing sensitivity of experimental techniques more and more complex species will be detected in future in the ice. In addition, a statistical interpretation in terms of Monte-Carlo simulations, allows an extension of conclusions beyond experimental possibilities.

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