

NASA LAW, February 14-16, 2006, UNLV, Las Vegas

Laboratory experiments on interstellar ice analogs: The sticking and desorption of small physisorbed molecules

G. W. Fuchs¹, K. Acharyya², S. E. Bisschop¹, K. I. Öberg¹, F. A. van Broekhuizen¹, H. J. Fraser³, S. Schlemmer⁴, E. F. van Dishoeck¹, & H. Linnartz¹

¹*Raymond and Beverly Sackler Laboratory for Astrophysics at Leiden Observatory, The Netherlands,* ²*Center For Space Physics, Kolkata, India,* ³*Department of Physics, University of Strathclyde, Scotland,* ⁴*I. Physikalisches Institut, University of Cologne, Germany*

fuchs@strw.leidenuniv.nl

ABSTRACT

Molecular oxygen and nitrogen are difficult to observe since they are infrared inactive and radio quiet. The low O₂ abundances found so far combined with general considerations of dense cloud conditions suggest molecular oxygen is frozen out at low temperatures (< 20 K) in the shielded inner regions of cloud cores. In solid form O₂ and N₂ can only be observed as adjuncts within other ice constituents, like CO. In this work we focus on fundamental properties of N₂ and O₂ in CO ice-gas systems, e.g. desorption characteristics and sticking probabilities at low temperatures for different ice morphologies.

1. Introduction

The understanding of dense cloud and pre-stellar core chemistry depends strongly on the available molecule budget and distribution. This is particularly true for oxygen and nitrogen. Since O₂ nor N₂ has an electric dipole moment direct observations of these species in cold environments are difficult and abundances are uncertain. Nevertheless, the low values that have been derived from SWAS and ODIN observations of the order $N(\text{O}_2)/N(\text{H}_2) \approx 10^{-7} - 10^{-8}$ for gas phase O₂ raise questions on the total oxygen budget, especially when compared with atomic oxygen abundances observed towards diffuse clouds. It is believed that at high enough densities ($n(\text{H}_2)=10^6-10^8 \text{ cm}^{-3}$) and low enough temperatures (10-30

¹Correspondence to: G. W. Fuchs

K) even volatile molecules like CO, N₂ and O₂ are removed from the gas-phase by freeze-out processes on grains, thus building interstellar ices. These freeze-out processes can also significantly influence the chemistry. For example, since CO is one of the main destroyers of N₂H⁺ a different freeze-out temperature of CO and N₂ would alter any subsequent reaction of N₂H⁺. An anti-correlation between C¹⁸O and N₂H⁺ can be observed towards the B68 pre-stellar cloud and it has been suggested that different sticking probabilities or binding energies between CO and N₂ (the parent molecule of N₂H⁺) are responsible for this effect (Flower *et al.* 2005; Bergin *et al.* 2002). Experiments in the laboratory help clarifying the situation by measuring key properties of ice-gas interactions, like the sticking probability, desorption kinetics and binding energies of the species.

2. Experiment

Experiments have been performed using the CRYOPAD ultra-high vacuum set-up previously described in van Broekhuizen 2005 and Fuchs *et al.* 2006. CO, N₂ and O₂ have been deposited on a poly-crystalline gold surface at 14 K in mixed and layered structures forming amorphous ices. For astrophysical relevance, ices between 10 and 160 mono-layer thickness have been investigated using TPD (Temperature Programmed Desorption) techniques. The TPD spectra are used to determine the binding energies and desorption kinetics of these species under various conditions. They also give insight into the underlying intermolecular interactions. The TPD were taken by a controlled linear warm up ($dT/dt = 0.1$ K/min) of the ices between 14 and 80 K during which the evaporated molecules have been monitored by a quadrupole mass spectrometer. Simultaneously reflection absorption infrared (RAIR) spectra have been recorded using a Fourier Transform infrared spectrometer to investigate changes in the ice structure. The RAIR data have been discussed in Fuchs *et al.* 2006 and aid the modeling of the TPD data.

3. Results

The experiments have been discussed in Fuchs *et al.* 2006 and Öberg *et al.* 2005, Bisschop *et al.* 2006, Acharyya *et al.* 2006. To elucidate the anti-correlation problem between CO and N₂H⁺ and also to confirm whether O₂ might be frozen out on grains the sticking coefficients S for CO sticking on CO, N₂ on CO, O₂ on O₂, etc. have been determined. It has been found that all sticking coefficients at 15 K have similar values and that their lower limit value is around 0.9, thus verifying the assumption $S=1$ made by most modelers. Hence, O₂ can easily freeze out below 20 K in dense cores and the anti-correlation between CO and N₂H⁺ is not due to different sticking coefficients of N₂ and CO. TPD spectra have been recorded for pure O₂, CO and N₂ and analyzed using Polanyi-Wigner type rate equations, e.g. to determine the desorption energies E_d . It has been found that

$E_d(\text{O}_2) > E_d(\text{CO}) > E_d(\text{N}_2)$, with $E_d(\text{O}_2) \approx 925$ K, $E_d(\text{CO}) \approx 855$ K and $E_d(\text{N}_2) \approx 790$ K using 0th-order desorption kinetics. Layered and mixed CO-O₂ ices reveal similar TPD spectra with respect to pure ices but the desorption energies of the O₂ in these cases are lowered by 10 K whereas the E_d for CO is increased by 15 K. No significant co-desorption of CO with O₂ can be observed (Acharyya *et al.* 2006). In contrast, CO-N₂ ices show co-desorption of N₂ with CO for layered and mixed ices. Thus, the CO-N₂ ice system reveals a two-step desorption process for the N₂ molecule involving 0th- and 1st-order kinetics due to diffusion and a sufficiently large E_d energy separation between the N₂-N₂ binding sites and the N₂-CO type binding sites (Bisschop *et al.* 2006).

Both N₂ and O₂ interact with CO mainly due to quadrupole interaction with quadrupole moments of $Q(\text{N}_2) \lesssim Q(\text{CO})$ and $Q(\text{O}_2) \ll Q(\text{N}_2)$. Furthermore, CO and N₂ have the same crystalline structure below 30 K whereas O₂ possesses a different crystalline architecture. Thus, N₂ can interact well with CO, i.e. stick, mix and co-desorb, whereas O₂ cannot. This follows the more general idea that desorption processes can be classified according to their intermolecular interaction pattern and crystalline structures. For example, CO, N₂ and O₂ in water ice behave differently (Collings *et al.* 2004, see their Fig. 3) causing CO to desorb at higher temperatures than O₂ (around 30-50 K)

4. Astrophysical implications

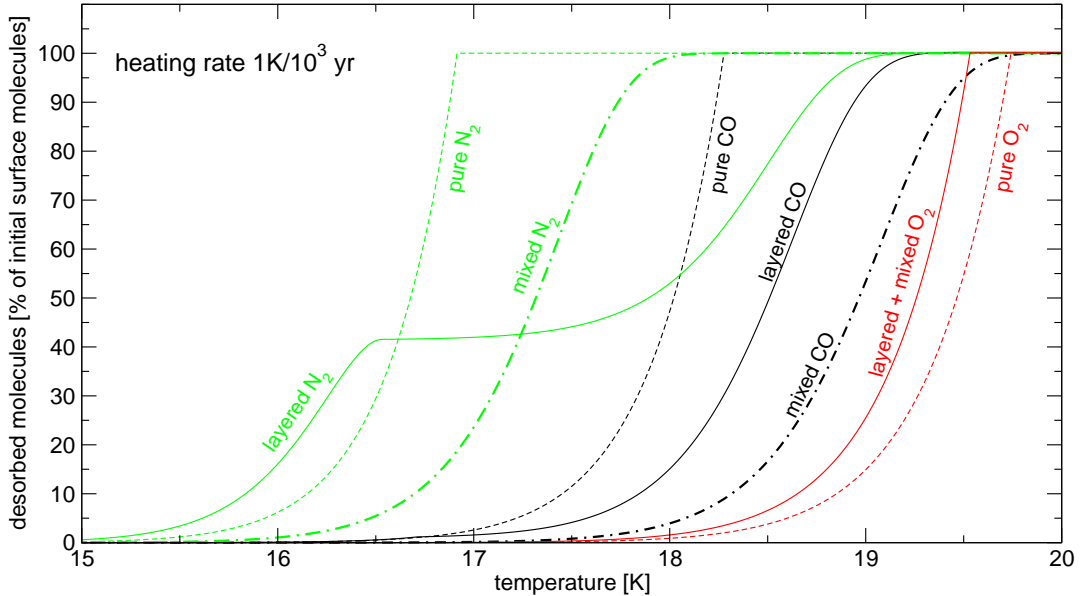


Fig. 1.— Desorption on astrophysical timescales (1 K/10³ yr) starting at 10 K and assuming 40 monolayer of pure, mixed or layered O₂, CO, N₂ ice (i.e. no accretion has been considered).

The experimental data have been incorporated in an empirical kinetic model to predict desorption rates at a typical warm up rate ($dT/dt = 1\text{K}/10^3\text{ yr}$) for a newly born star (Fig. 1). N_2 desorbs first, then CO followed by O_2 at the highest temperatures. Independent of the ice morphology, oxygen molecules desorb mainly between 18.5 and 20 K. CO is more volatile and also has a wider desorption temperature range showing larger differences between pure, mixed and layered CO ices. Most remarkably is N_2 which in its layered CO- N_2 form desorbs in two steps covering a desorption range of 4 K between 15 and 19 K. Overall the desorption takes place within 5 K for all species, i.e. equivalent to only 5000 yr of the evolutionary stage of the star, and can thus hardly make up for the observed anti-correlation between CO and N_2H^+ . Although O_2 can well be frozen out in dense cores it has not been seen in the later stages of star formation, e.g. in hot cores, probably due to beam dilution effects. Future deep searches for O_2 with the HERSCHEL Space Observatory will be able to put stringent limits on the gaseous O_2 abundance.

This work has been supported by NOVA and a NWO Spinoza grant.

REFERENCES

- Acharyya *et al.* 2006, *Astron.&Astrophys.*, in prep.
Bergin *et al.* 2002, *Astrophys.J.*, 570, L101
Bisschop *et al.*, 2006, *Astron.&Astrophys.*, in press, (see astro-ph/0601082)
Collings *et al.* 2004, *Mon.Not.R.Astron.Soc.*, 354, 1133
Flower *et al.* 2005, *Astron.&Astrophys.*, 436, 933
Fuchs *et al.* 2006, *Faraday Discuss.*, in press (DOI:10.1039/B517262B)
Öberg *et al.* 2005, *Astrophys.J.Lett.* 621, L33.
van Broekhuizen 2005, PhD thesis, Leiden University