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CO_2 trapping in amorphous H_2O ice: Relevance to polar mesospheric cloud particles

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ABSTRACT

Polar mesospheric clouds form in the summer high latitude mesopause region and are primarily comprised of H_2O ice, forming at temperatures below 150 K. Average summertime temperatures in the polar mesosphere (78°N) are approximately 125 K and can be driven lower than 100 K by gravity waves. Under these extreme temperature conditions and given the relative mesospheric concentrations of CO_2 and H_2O ($\sim$360 ppmv and $\sim$10 ppmv, respectively) it has been hypothesised that CO_2 molecules could become trapped within amorphous mesospheric ice particles, possibly making a significant contribution to the total condensed volume. Studies of CO_2 trapping in co-deposited gas mixtures of increasing CO_2:H_2O ratio (deposited at 98 K) were analysed *via* temperature programmed desorption. CO_2 trapping was found to be negligible when the H_2O flux to the surface was reduced to 4.8×10^{13} molecules cm^{-2} s^{-1}. This corresponds to an average of 0.4 H_2O molecules depositing on an adsorbed CO_2 molecule and thereby trapping it in amorphous ice. Extrapolating the experimental data to mesospheric conditions shows that a mesospheric temperature of 100 K would be required (at a maximum mesospheric H_2O concentration of 10 ppmv) in order to trap CO_2 in the ice particles. Given the rarity of this temperature being reached in the mesosphere, this process would be an unlikely occurrence.

1. Introduction

Polar mesospheric clouds (PMCs) (also known as noctilucent clouds) are optically thin clouds that form in the summer polar mesopause region. PMCs primarily consist of small H_2O ice particles with median radii of $\sim$51 nm (von Cossart et al., 1999; Hervig et al., 2001), which can form when the temperature falls below the water frost point (150 K). Larger ice particles which sediment to the bottom of the ice layer, at altitudes between 82 and 85 km, scatter sufficient light to become optically visible (Rapp and Thomas, 2006).

A major source of ice nuclei for heterogeneous nucleation in the mesosphere are meteoric smoke particles (MSPs) (Rapp and Thomas, 2006; Plane, 2011). MSPs are a product of ablation and subsequent recondensation of meteoric material (Saunders and Plane, 2006), of which somewhere between 10 and 110 tonnes enters the atmosphere daily (Plane, 2012). Average temperatures in the high latitude upper mesosphere (78°N) during summertime are approximately 125 K, while gravity waves can drive temperatures lower than 100 K (Lübken et al., 2009). Murray and Jensen (2010) showed that homogeneous nucleation may also be possible under extreme mesospheric temperature conditions below 110 K. These authors also suggested that amorphous ice may preferentially nucleate due to a lower energy barrier to nucleation compared to crystalline ice. Satellite measurements indicate PMCs are composed primarily of crystalline ice but could not rule out amorphous ice formation (Hervig and Gordley, 2010).

H_2O is present in the high latitude mesopause during the summertime at concentrations of up to 10 ppmv (Rong et al., 2010). The source of H_2O vapour in the mesosphere is due to a combination of atmospheric upwelling and methane oxidation via reaction with $O(^1D)$ and OH radicals (Thomas, 1991). CO_2 is well mixed vertically with concentrations $>$360 ppmv up to altitudes of approximately 80 km, above which UV photolysis of CO_2 (to CO and O) and gravitational separation with respect to lighter gas species become dominant removal processes. Due to increasing anthropogenic sources of CO_2, a global decadal increase of 23.5 ± 6.3 ppmv is currently observed (Emmert et al., 2012). Given the concentrations of trace species present in the mesosphere during the PMC cloud season and the extreme low temperatures, it is possible that CO_2 trapping in amorphous solid water (ASW) ice could be a viable process. However, it should be noted CO_2 cannot become trapped when ASW has irreversibly crystallised to crystalline solid water (CSW) ice, or when ice is initially deposited as CSW ice.

CO_2 trapping in ASW ice has been experimentally observed

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under conditions relevant to the interstellar medium (ISM) (Galvez et al., 2007; Malyk et al., 2007; Mate et al., 2008). However, these studies looked at deposition temperatures below atmospheric relevance (≤ 90 K) and low CO_2:H_2O ratios (~0.02:1 to 0.7:1) due to the composition of interstellar ice. Experimental studies have also investigated CO_2 trapping in the Martian regolith (Trainer et al., 2010), but these were at higher temperatures and pressures than those observed during the PMC cloud season. To our knowledge, studies of co-deposition of high CO_2:H_2O ratio gas mixtures at conditions relevant to the Earth's mesosphere have not been performed. In the present study, the co-deposition of high CO_2:H_2O ratio mixtures were studied using temperature programmed desorption (TPD) to determine the mesospheric conditions under which CO_2 trapping in ASW ice would be possible. The experimental procedure is described in Section 2, and the results and discussion in Section 3.

2. Experimental procedure

The experiments were undertaken in an ultra-high vacuum (UHV) chamber with an internal volume of ~25 L (see Fig. 1). This system has been previously described by Vondrak et al. (2006). Briefly, the chamber is pumped *via* a 550 L s^{-1} turbo-molecular pump (Varian Turbo-V 551 Navigator) backed by a rotary pump (Varian, DS302), achieving a base pressure of typically $< 7 \times 10^{-10}$ mbar. The chamber is equipped with a quadrupole mass spectrometer (QMS) (Hiden, HAL 3F 301 RC PIC), a needle valve (NUPRO, SS4BK) for gas dosing and an inert ion (Ar^+) sputter source (PSP technology Ltd., ISIS 3000) which was modified to function as a leak valve for this study. Within the centre of the UHV chamber is a cylindrical Cu (111) crystal sample of 12 mm diameter and 2.5 mm thickness, polished to 1 μm and oriented to ± 0.5° of the (111) plane. The crystal is mounted *via* tungsten (W) heating wires onto an oxygen free high conductivity (OFHC) cold finger (shown in Fig. 1), which in turn is mounted onto an xyzθ manipulator. The sample is liquid nitrogen cooled to a base temperature of approximately 98 K and can be heated resistively by the W wires embedded in the perimeter of the Cu (111) crystal. The surface temperature is monitored using a K-type thermocouple positioned in a small hole on the side of the Cu (111) crystal. Prior to each experiment the Cu (111) crystal was annealed to 800 K for 30 min.

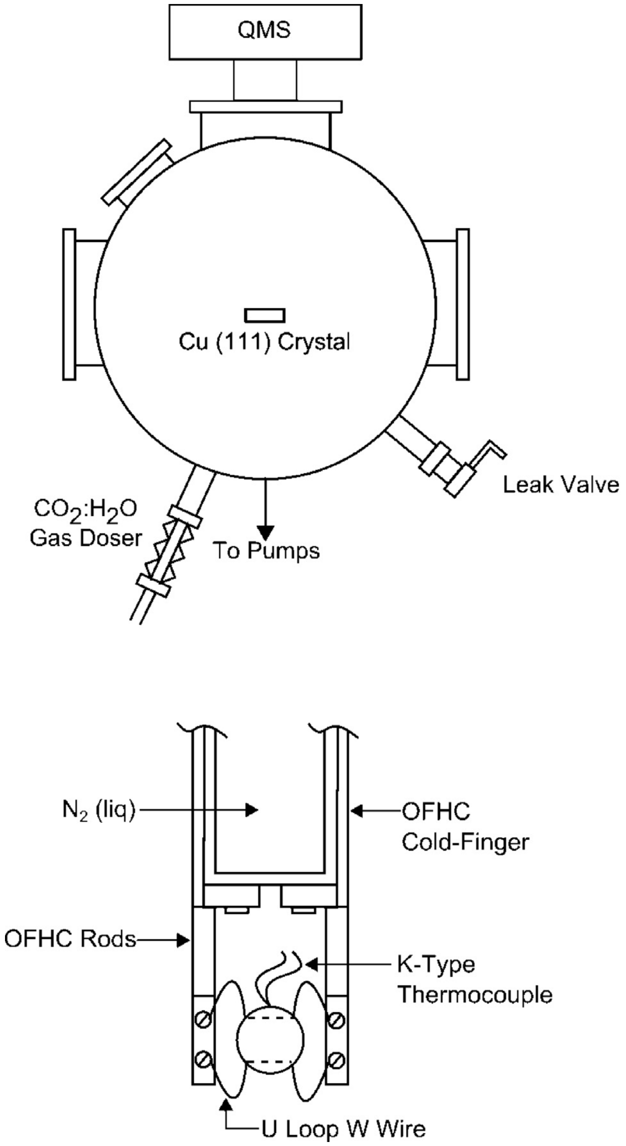

Fig. 1. Schematic diagram of the UHV chamber upper level (top) and Cu (111) crystal mount (bottom).

H_2O (deionised) was subject to three freeze-pump-thaw cycles and CO_2 (from dry ice) was first purified by pumping. CO_2:H_2O gas mixtures at ratios varying from 1:1 to 13:1 were prepared using manometric techniques on a glass gas-handling line, and then dosed onto the Cu (111) crystal *via* the needle valve in the form of a collimated effusive beam. This beam has a diameter only slightly larger than the Cu (111) crystal and therefore minimises adsorption (and therefore desorption) of either species onto other nearby surfaces such as the OFHC cold finger (see Fig. 1). Any species adsorbed onto the W wires would desorb immediately upon heating. The dosing rates were calibrated for CO_2 and H_2O separately through beam flux calibrations based on the procedure of Oakes (1994). Briefly, the beam flux (F_{beam}) is calculated from the exponential decay of a gas species from the point where the input gas flow has been terminated. The exponential decay is described by:

$$P = P_0 \exp^{-C_m t} \tag{1}$$

where P is the pressure, P_0 is the initial pressure at the termination of the dose, C_m is the pumping coefficient for the gas and t is the time from the start of the decay. Eq. (1) was linearised and C_m obtained from the gradient. From this F_{beam} is given by:

$$F_{beam} = \frac{V_{system} C_m P_0}{k_B T A_{beam}} \tag{2}$$

where V_{system} is the volume of the chamber, k_B is the Boltzmann constant, T the temperature of the gaseous species and A_{beam} the cross sectional area of the molecular beam. The CO_2 and H_2O fluxes varied from $(3.4 \ –6.3) \times 10^{14}$ molecules cm^{-2} s^{-1} and $(0.5–3.4) \times 10^{14}$ molecules cm^{-2} s^{-1}, respectively. The total flux of CO_2 and H_2O remained the same (within experimental error) for all the experiments (6.8×10^{14} molecules cm^{-2} s^{-1}).

In a typical experiment, the gas mixture was dosed for 7200 s onto the Cu (111) crystal at a base temperature of 98 K. This enabled the H_2O film to form as ASW ice. The absorbed species were then analysed *via* TPD, where the Cu crystal was heated between 98 and 200 K at a heating ramp of 0.25 K s^{-1}. This ensured that all dosed species had desorbed. The CO_2 TPD profiles described in the following section were corrected against a pure CO_2 TPD trace to remove the surface CO_2 desorption. This surface CO_2 is weakly physisorbed to the ASW ice surface and rapidly desorbs upon sample heating, peaking at temperatures of approximately 125 K, which is more than 20 K lower than the observed initial