

H₂O and CO₂ vapor pressure measurements at temperatures relevant to the middle atmosphere of Earth and Mars

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Abstract

Measurements of the vapor pressure of H₂O and CO₂ at temperatures relevant to the middle atmosphere of Earth and Mars are rare but important in order to describe cloud formation and ice particle growth processes. In this contribution we present a novel technique for measuring the vapor pressure of condensable gases by analyzing the depositional growth rates on free nanoparticles at high supersaturation. The method is applied to measure the vapor pressure of CO₂ between 75K and 85K. By comparison with previous measurements and parameterizations we are able to show the excellent functionality of the method. In addition, the method is used to measure the vapor pressure over H₂O ice between 135K and 160K. We show that the vapor pressure of so called stacking disordered ice I_{sd} deposited at temperatures below 160K is significantly higher compared to hexagonal ice I_h. The consequences for ice cloud formation in the atmosphere of Earth and Mars will be discussed.

1. Introduction

Measurements of the vapor pressure of H₂O and CO₂ at temperatures relevant to the middle atmosphere of Earth and Mars are rare but important in order to predict conditions for H₂O and CO₂ cloud formation and ice particle growth processes. Whereas CO₂ is known to have one phase down to a temperature of about 50K [5], water ice can in addition to the well characterized and stable hexagonal ice I_h freeze in different metastable forms. At temperatures relevant to the middle atmosphere of Earth and Mars, water has been identified to form so called stacking disordered ice I_{sd} [e.g. 7], and below about 120K amorphous ice I_a [e.g. 4]. The vapor pressure of I_a has been determined to be about 3 times larger as compared to I_{sd} [e.g. 10]. Due to heat capacity

measurements [e.g. 11] and direct pressure measurements between 180K and 190K [9], the vapor pressure of I_{sd} is believed to be about 10% to 15% higher as compared to I_h [8]. However, high quality vapor pressure measurements of I_{sd} at temperatures below 160K do not exist and are eminent in order to proof the expected difference in the vapor pressures of I_{sd} and I_h.

Recently, we introduced a novel experimental setup [2, 6] specifically designed for the investigation of adsorption, nucleation and subsequent depositional growth of H₂O and CO₂ on nanoparticles at temperatures relevant to the middle atmosphere of Earth and Mars. Analyzing the CO₂ and H₂O ice growth rate of the particles at high saturation ($S > 1000$) allows us to determine the vapor pressure at the investigated temperatures.

2. Experimental Method

Singly charged nanometer size iron oxide and silica particles are produced in a microwave plasma particle source and directly transferred into the TRAPS vacuum system [6]. The particles are size selected and accumulated in the novel supersaturation chamber and ion trap MICE [2]. In MICE, the particles are exposed to realistic mesospheric conditions in terms of background pressure and temperature as well as CO₂ and H₂O vapor concentrations. The vapor pressures of CO₂ and H₂O are adjusted by controlling the temperature and therefore the sublimation speed of molecules from CO₂ or H₂O covered surfaces. From MICE we extract a small amount of the trapped particle population at periodic time steps and analyze their mass distribution with a time-of-flight mass spectrometer. By observing CO₂ and H₂O growth rates on the nanoparticles at high S values ($S > 1000$) we are able to infer the sublimation rate and therefore

the vapor pressure of CO₂ and H₂O at the controlled surface temperature.

3. Results and Discussion

Figure 1 shows an exemplary measurement of H₂O deposition on a 2.5nm silica particle. The particle temperature has been kept to 129.7K. The surfaces supplying the flow of water molecules have been set to 156.7K.

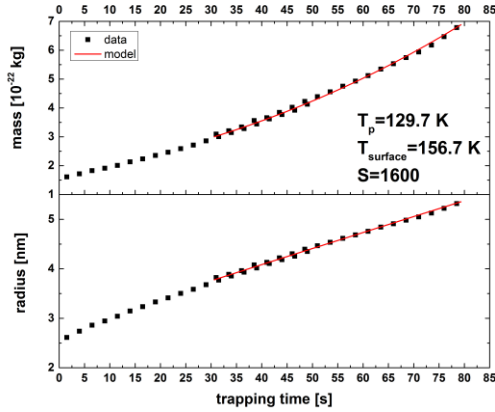


Figure 1: Exemplary measurement of H₂O ice growth on a 2.5nm silica particle at a Saturation of 1600

The H₂O ice growth rate of the nanoparticles can be expressed by the simple equation:

$$\frac{dm}{dt} = [\alpha \cdot j_{in} - j_{out}(t)] \cdot A_c(t) \cdot m_{H_2O} \quad (1)$$

Here, m_{H_2O} is the mass of one water molecule and $A_c(t)$ is the effective surface area which describes the collision between the particle and a water molecule. The sticking coefficient α has been determined to 1 for CO₂ [3] as well as H₂O [1] at investigated particle temperatures. The outgoing flow j_{out} can be calculated according to the Kelvin effect. However, at S values above 1000, uncertainties in calculating j_{out} become less significant. The red curve in Figure 1 represents a numerical fit of j_{in} in Eq. 1. By knowing the geometry of MICE [2], j_{in} can be used to calculate the vapor pressure at the temperature of the surfaces providing the water molecule flow.

We will present results of the vapor pressure measurements for CO₂ between 75K and 85K. These measurements are compared to existing

measurements and CO₂ vapor pressure parameterizations at these temperatures. We conclude that analyzing growth rates on nanoparticles in MICE at high S values is a very sensitive technique to measure the vapor pressure if the sticking coefficient is known. In addition we show determined vapor pressures of I_{sd} between 135K and 160K and conclude that the vapor pressure of I_{sd} might be significantly increased in respect to I_h and discuss its consequences to water ice cloud formation in the atmosphere of Earth and Mars.

Acknowledgements

The authors thank the German Federal Ministry of Education and Research (BMBF, grant number 05K13VH3) and the German Research Foundation (DFG, grant number LE 834/4-1) for financial support of this work.

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