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FTIR-Spectroscopic Studies of Polar Stratospheric Cloud Model Surfaces: Characterization of Nitric Acid Hydrates and Heterogeneous Reactions Involving N_2O_5 and HBr

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FTIR-spectroscopy has been applied to study model surfaces and processes on cold surfaces which are related to the role of polar stratospheric clouds (PSC's) in ozone depletion in polar regions:

(i) Thin solid films of nitric acid hydrates were prepared by deposition of gas-phase HNO_3 and H_2O on a cold substrate. Hydrates of HNO_3 have been found to be major components of PSC's (type I). In our investigations the mono- and the dihydrate as well as the two modifications of nitric acid trihydrate, α - and β -NAT, were obtained and characterized by their FTIR-spectra.

(ii) The heterogeneous reaction between gas-phase H_2O and solid, ionic N_2O_5 leads to the formation of both the α - and β - modifications of NAT.

(iii) Gas-phase HBr is hydrolyzed on the surface of a water ice film resulting in the formation of amorphous and crystalline hydrogen bromide monohydrates.

1. INTRODUCTION

Polar stratospheric clouds (PSC's) are formed at low temperatures (below 195 K) in the wintery polar stratosphere. The most frequently observed PSC's are of type I and are believed to consist primarily of *nitric acid trihydrate* (NAT). At even lower temperatures particles consisting of pure water ice (PSC's type II) are formed. It is now well established that heterogeneous reactions on the surfaces of PSC's convert reservoir halogen compounds (e.g. ClONO_2) to active species (e.g. Cl_2) which are believed to cause enhanced ozone depletion at the end of the polar night [1]. Nitrogen compounds (NO_x) which in turn deactivate active halogen species are efficiently removed from the gas phase by these reactions [1].

We have examined the formation and spectral characteristics of the different nitric acid hydrates in order to obtain reference spectra for the study of heterogeneous reactions on PSC model surfaces.

The study of an important stratospheric denitrification process, which involves the principal nighttime reservoir species of NO_x , dinitrogenpentoxide, has been one of the main goals of our investigations:



Furthermore, we have studied the adsorption of the bromine reservoir species HBr on pure water ices, which represent model surfaces of PSC's type II.

2. EXPERIMENTAL

The solid samples were prepared by depositing the compounds from the gas phase onto an optically polished aluminium plate which is cooled by a LN₂ cryostat and placed inside an evacuated chamber. Heterogeneous processes were studied by passing a continuous flow of gas (e.g. HBr) onto the solid sample surface. With a set of reflecting mirrors the infrared beam of the attached FTIR-spectrometer (model IFS 66v, Bruker (Karlsruhe)) is focussed onto the substrate to enable the registration of Reflection Absorption InfraRed (RAIR) spectra of the solid sample films. The spectra were recorded at a resolution of 0.5 cm⁻¹ using a KBr/Ge beamsplitter and a LN₂ cooled MCT detector in the spectral range from 4000 cm⁻¹ to 500 cm⁻¹.

3. RESULTS AND DISCUSSION

3.1 Nitric Acid Hydrates

We have prepared nitric acid monohydrate (NAM), nitric acid dihydrate (NAD) and nitric acid trihydrate (NAT). NAT was found to be the product in the processes described below. The spectroscopic features which we have observed for the trihydrate will be described in the following.

Nitric acid trihydrate exists in two different modifications, which are denoted α - and β -NAT [2,3]. In both modifications the nitric acid is completely in its ionic form. α -NAT was obtained either by annealing an amorphous solid of HNO₃/H₂O (1:3) from 77 K to 180 K, or by fast deposition of a HNO₃/H₂O (1:3) gas mixture from the gas phase at 175 K. The solid film composed of the α -modification changed to β -NAT by annealing to 185 K. The specific absorptions of α - and β -NAT are in accordance with literature data [2] and are depicted in figure 1. The broad absorption bands between 3000 cm⁻¹ and 1700 cm⁻¹ are assigned to the modes of H₃O⁺ (ν_3 , ν_1 and ν_4). The asymmetric stretching vibration ν_3 of NO₃⁻ is observed at 1365 cm⁻¹ (α -NAT) and 1330 cm⁻¹ (β -NAT). Intense bands arising from weakly hydrogen bonded OH-groups are observed at 3427 cm⁻¹ (α -NAT) and 3365 cm⁻¹ (β -NAT) beside the typical OH-stretching bands of water aggregates (3210 cm⁻¹).

It should be mentioned that there is also experimental evidence that beside NAT the dihydrate (NAD) has to be taken into account as a further possible component of PSC's type I [2].

3.2 Reaction between solid N₂O₅ and gas-phase H₂O

A thin film of ionic N₂O₅ was exposed to a gas-phase flow of H₂O in order to study how the product in reaction 1 (HNO₃) is stabilized in the presence of excess water. It has been recently shown that no reaction takes place below 160 K when N₂O₅ is in the ionic form [4]. In our studies we have found that reaction 1 does readily take place at N₂O₅ temperatures above 167 K [3].

When the experiment was performed at 168 K the N₂O₅ absorption bands (ν_3 (NO₂⁺) at 2375 cm⁻¹, ν_3 (NO₃⁻) at 1380 cm⁻¹) decreased, accompanied by a strong increase of bands which can be unambiguously assigned to α -NAT. A difference spectrum obtained by subtracting the spectra recorded before and after exposing the N₂O₅ film to gas-phase H₂O at 168 K is shown in figure 2a. The same experiment, performed at a slightly higher temperature (169 K), leads to the formation of β -NAT as illustrated in figure 2b.

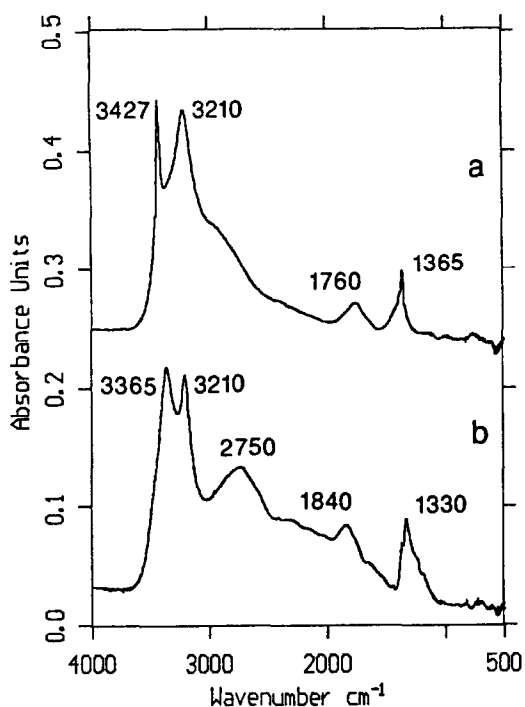


Figure 1. FTIR-spectra of thin solid films of α -NAT (a) and β -NAT (b). Spectra have been recorded at 175 K (a) and 185 K (b).

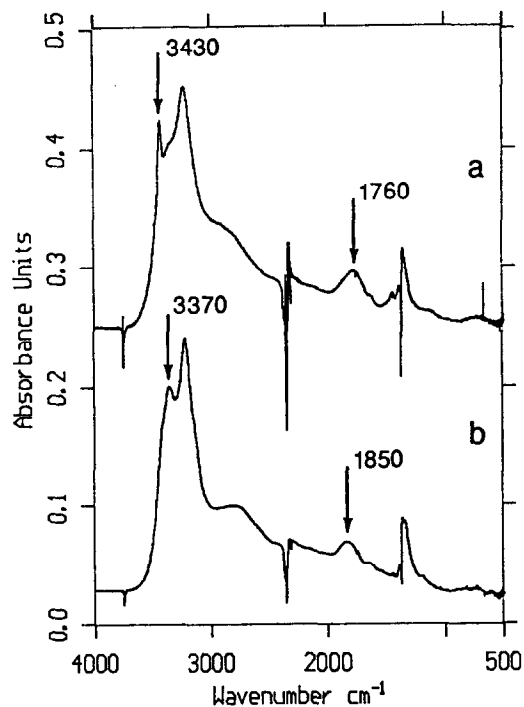


Figure 2. FTIR-difference spectra resulting from the exposure of thin solid N_2O_5 films to gas-phase H_2O . The temperatures of the films have been 168 K (a) and 169 K (b).

3.3 Reaction of gaseous HBr on water ice surfaces

The spectrum of a pure ice film is shown in figure 3a. It is dominated by the strong $\nu_{1,3}$ OH-stretching absorptions covering the range 3500 to 3000 cm^{-1} . After the exposure of the ice surface ($T = 90$ K) to a continuous flow of gaseous HBr new features appeared in the spectrum (see figure 3b). Due to the formation of solvated and strongly H-bonded ionic HBr species the overall absorption below ~ 3000 cm^{-1} increases. A strong band with the maximum at 2595 cm^{-1} is observed and assigned to an amorphous 1:1 hydrate in agreement with Delzeit et al. [6].



After annealing of the sample the amorphous hydrate converted into a crystalline monohydrate. The band at ~ 2800 cm^{-1} in figure 3c can be attributed to the stretching modes of the hydronium ion. The absorption bands at 1662 cm^{-1} and 2075 cm^{-1} are assigned to the bending modes of H_3O^+ ν_4 and $(\nu_4 + \nu_2)$. Weakly physisorbed molecular HBr, which should reveal a distinct band at ~ 2450 cm^{-1} has not been observed in our experiments. Thus, it can be concluded that the 1:1 hydrates are largely in their ionized form and that the band at ~ 2590 cm^{-1} results from H-bonding of H_3O^+ with the neighbor Br^- ion. The results indicate, that hydrolysis of hydrogen bromide or hydrogen chloride has to be taken into account in heterogeneous reactions of HBr or HCl on surfaces of PSC's type II [5, 6].

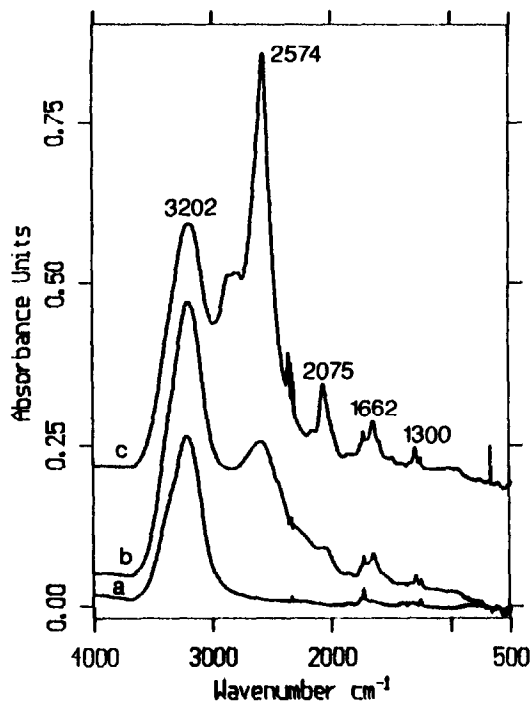


Figure 3. FTIR-spectra of a water ice film ($T = 90\text{K}$) recorded before (a) and after (b) the exposure to HBr; (c) shows the spectrum after annealing of the samples to 140 K.

4. CONCLUSIONS

Our experiments allow the following conclusions:

- (i) the surfaces of PSC type II particles, consisting mainly of water ice, can be converted to PSC type I like surfaces by the reaction of N_2O_5 on ice surfaces. In the stratosphere such a process could therefore prolong the lifetime of the particles because the evaporation point of NAT is 5 to 7 K above that of pure ice. It should also influence the reaction probabilities of the other important heterogeneous reactions (e.g. $\text{ClONO}_2 + \text{H}_2\text{O}$) taking place on the surfaces of particles in the stratosphere.
- (ii) ionic chemistry is very important in the heterogeneous processes even at the low temperatures of the wintery stratosphere as all the condensed phase products in our experiments were in the ionic state.

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