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Adsorption and reactions of atmospheric constituents and pollutants on ice particles: an FTIR study

A.V. Rudakova, I.L. Marinov, M.S. Poretskiy, and A.A. Tsyganenko

V.A. Fock Institute of Physics, Department of Physics, St.Petersburg State University, St.Petersburg, Russia 198504

Processes on icy particles attract much attention due to their importance for atmospheric science, ecology and astrophysics. In this work, adsorption and ecologically important reactions of some molecules on pure and mixed water icy films by means of FTIR spectroscopy have been investigated.

The cell for spectral studies of adsorbed molecules at variable temperatures (55-370 K), described elsewhere1, enables one to run the spectra in the presence of gaseous adsorbate, and even to perform adsorption from the solution in some cryogenic solvents. For the studies of ice films, it was equipped with a device for water vapour sputtering from the heated capillaries and deposition onto the inner BaF2 or ZnSe windows of the cell, cooled by liquid nitrogen. Lower temperatures were obtained by pumping off evaporating nitrogen from the coolant volume. The estimated specific surface area of freshly deposited at 77 K water ice film was about 160 m2/g and decreases on raising the temperature together with the diminishing intensity of the bands of dangling OH (OD) groups at 3696 (2727) cm-1 until the latter disappear at 130 – 160 K when the changes of bulk absorption provide evidence for a phase transition from amorphous to polycrystalline ice. CO adsorption at 77 K results in two bands at 2153 and 2137 cm-1 assigned to molecules forming weak H-bond with the dangling hydroxyl groups and bound to unsaturated surface oxygen atoms, respectively2. The band of dangling hydroxyl groups moves to lower wavenumbers on adsorption of different molecules (hydrogen, nitrogen, methane, ozone, NO, ethane or chlorinated ethenes, etc.). The shift value depends on the nature of adsorbate. Besides this shift, spectra of adsorbed nitrogen and methane registered at 55 K reveal the adsorption intensity decrease at ∼ 2650 cm-1 at the high-frequency slope of bulk adsorption, and increase at about 25 cm-1 below. We interpret this perturbation as a strengthening of H-bonds between surface water molecules, which act as adsorption sites either as a proton-donor or as a donor of the lone pair of electrons. Such adsorption-induced relaxation explains the dependence of physico-chemical properties of icy particles on the presence of atmospheric gases.

Spectra HCN/D2O and ND3/D2O mixed icy films with low (1:10) dopant/water ratios do not manifest any changes in the acidic or basic properties of dangling hydroxyl groups or surface oxygen atoms, but reveal a difference in the proportion between the concentrations of these sites as compared with that for pure water ice. For high dopant concentrations (1:1), the dangling hydroxyls were not observed; the dominant adsorption sites for CO are likely to be the unsaturated oxygen atoms, while serious structural changes occur in the bulk of ices.

Ecologically important reactions of atmospheric pollutants such as ozonolysis of ethene, chlorinated ethenes, hydrogen cyanide, and methyl bromide adsorbed on water ice film as well as the influence of UV radiation on this process have been studied in 77 – 200 K temperature range by FTIR spectroscopy. Ozone co-adsorption with ethene or C2H3Cl readily leads to ozonolysis reaction, which also starts for C2H2Cl2 isomers but only at temperatures elevated up to 120 – 150 K. Co-adsorption of O3 with HCN or CH3Br molecules in the dark does not lead to any noticeable spectral changes. Irradiation of HCN or CH3Br deposited on ice films in the presence of ozone leads to appearance of new bands revealing the formation of ozonolysis products. The same "synergetic effect" of simultaneous action of ozone and UV radiation at 77 K, was found for C2H2Cl2 isomers and C2Cl4, which are resistant against O3 even at higher temperatures. The obtained spectral dependence of photo-ozonolysis of C2Cl4 and HCN at 77 K shows that photoexcitation or photodissociation of ozone, evidently, accounts for the observed processes. The surface of ice particles, thus, plays the role of a condenser of atmospheric pollutants and acts as a micro- photoreactor in the atmospheric chemistry.

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