INFLUENCE OF POLLUTANT GASES ON THE STRUCTURE AND DYNAMICS OF THE ICE SURFACE - IMPLICATIONS FOR THE ENVIRONMENT

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The interaction of HCl with crystalline water ice has attracted much attention since the mid 80's owing to its importance in heterogeneous reactions occurring on the surface of polar stratospheric clouds (PSC) involved in the annual depletion of both Antarctic and Arctic ozone [1,2]. Nowadays, the impact of ice in atmospheric chemistry remains a major uncertainty, owing to the fact that snow covers more than 50% of the northern hemisphere ground during winter, and that about half of the water mass condensed in clouds is made out of ice.

Numerous experimental studies of HCl-ice interactions have been undertaken since the mid 90's which have suggested that HCl uptake on ice is limited to about one monolayer surface coverage, probably because of the weak solubility of HCl in bulk ice [1]. However, most of the experiments were done at much lower temperatures than those currently considered in the stratosphere. Possible explanations are still uncertain and there is still a debate on the precise role of the ice surface with respect to HCl adsorption, solvation and incorporation into ice crystals. It is not perfectly known how HCl is incorporated into the ice lattice and how the ice lattice responds to the presence of HCl on structural and dynamical points of view. Among the relevant questions is whether the formation of a quasi-liquid layer (QLL) is required or not to explain the large HCl uptake by ice under stratospheric conditions, that is around 190-200 K. The existence of a QLL at the surface of ice in presence of HCl has been proposed by Molina [3] and Abbatt et al [1] to explain the solvation of HCl and the observed large HCl uptake by ice crystals.

The aim of the experiments we have undertaken at LLB is to contribute to this debate in order to understand the basic mechanisms of trace gases-ice interactions, their impact on the atmospheric chemistry and by consequences on the climate.

In a first step, we have characterized pure ice films on a structural and dynamical point of view. In a second step, we have studied the influence of HCl on the structure and dynamics of the ice films in the HCl monolayer coverage range. For that purpose, we have condensed ice films on the (100) MgO surfaces. This substrate allows the formation of an ice I_h crystalline film on top of a stable (3x2) water monolayer [3]. In order to have a good signal/noise ratio, we have used very uniform MgO powders featuring micro-cubes exposing (100) facets only. These powders have been used many times for monolayer adsorption studies showing properties very close to those of single crystal surfaces. The specific area of the powders is 10 m^2/g. We have limited the ice film thickness to 5 monolayers (ML) in order to avoid capillary condensation which would obscure the analysis of the neutron results. Furthermore, such a film thickness is comparable to the size of the simulation boxes used in our molecular dynamics calculations.

The neutron experiments have been performed on the G6.1 diffractometer for the structure determination and on the Time of Flight (TOF) spectrometer G6.2 (Mibemol) for the dynamical studies.

I. Structure and dynamics of pure ice films [3]

The neutron diffraction spectrum performed at 190 K on a 5 ML thick D_2O ice film indicates the formation of hexagonal ice I_h. The (002) peak is broadened when compared to bulk ice, indicating the formation of a thin film with large (0001) planes. From the quasi-elastic neutron scattering spectra (QENS) we have determined, via diffusion models, the translational and orientational mobilities. No translational mobility (less than the detection limit D_t @ 10^{-6} cm^2 /s) has been detected below 250 K. Our QENS measurements indicate that a mobile layer showing a translational diffusion coefficient close to that of liquid water appears between 250 K and 265 K. Hence, one may reasonably infer that a surface melting transition occurs within this temperature range at about 10 K below that of the bulk melting point.

The experimental results are in qualitative agreement with molecular dynamics (MD)

simulations. Fig. 1 shows a snapshot of the supported ice film at T=220 K. One sees that the surface is perturbed : the QLL is observed with a shift of 30-40 K in the simulations compared to the experiments. This shift comes from the inaccuracy of the potential used in the simulations.

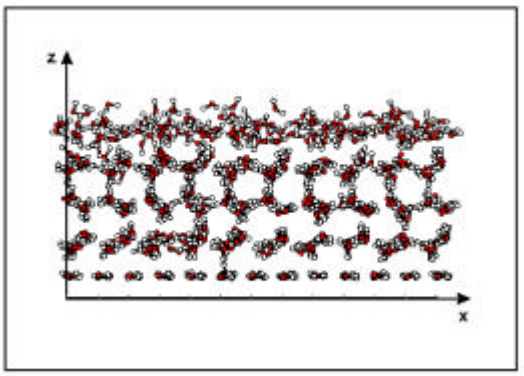

Figure 1. Snapshot of the supported ice film at T=220 K showing the MgO surface (z=0), the flat ice monolayer, and the hexagonal ice bilayers. One can see that the surface suffers strong disorder at this Temperature. Red and white circles represent oxygen and hydrogen atoms respectively

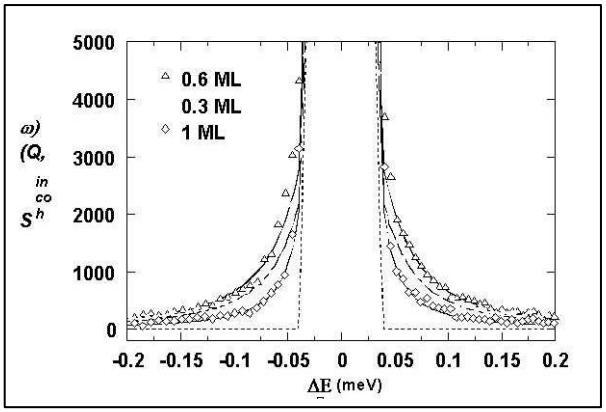

Figure 2. QENS spectra of the ice-HCl film at T=250 K showing broadening due to translational motion of water molecules in the ice film versus HCl coverage ($D_t = 0.8.10^{-5} cm^2/s$ for all coverages)

II. Influence of HCl adsorption [4,5]

The neutron-diffraction experiments conducted at T = 190K show clearly that, whatever the HCl coverage is, the structure I_h of the ice film appears to be unaffected by HCl adsorption, suggesting that HCl is mainly located at the surface and does not penetrate the film. This experimental result is in very good agreement with our MD calculations [5] showing that, at 190 K, 75% of the HCl molecules are trapped at the surface of the ice film, while the remaining 25% lie inside the outermost bilayer.

For an HCl coverage of 1 ML, hydrogen chloride dihydrate coexists with the hexagonal ice at T = 220 K. However, the absence of the (002) peak characteristic of bulk ice suggests that the ice I_h film is very thin. We interpret this feature by the fact that only one part of the film corresponds to the hydrate phase, while the other part corresponds to the ice I_h phase. As suggested by the MD calculations, at T ≥ 210K, HCl easily diffuses inside the ice film and destroys the ice I_h structure, except close to the MgO support where some order persists. At *T* = 250 K and 1 ML HCl, the diffractogram indicates that the ice/HCl film becomes an amorphous solid phase, which coexists with a small amount of liquid phase. As indicated by the QENS analysis (Fig. 2), the liquid proportion is weak under these conditions (≤ 9 %). For q_{HCl} = 0.3 and 0.6 ML, the liquid proportion found at *T* = 250 K (Fig. 2) corresponds to a film thickness of about one or two layers (namely, 30 and 45 % of the ice film thickness). MD calculations show that this mobility concerns preferentially the outermost layers, i.e. the occurrence of the surface premelting. *Hence, at submonolayer coverage, HCl is lowering the ice surface melting temperature by ~15 K compared to pure ice. Our experiments indicate that, at the lowest stratospheric temperature (T » 190 K), there is no quasi-liquid layer* having a translational mobility of a normal liquid at the ice surface. *Finally, the neutron experiments as well as the MD simulations are clearly showing that HCl is strongly perturbing the ice film in the temperature range of the troposphere, that is 230-260 K. That could be the case for other pollutants as well. Models of atmospheric chemistry will have to include these effects in order to explain the "in field" observations*, particularly in the upper troposphere and lower stratosphere where temperatures lie in the 220 K-260 K range.

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