ESRF	Experiment title :	Experiment number :
	HBr and HCl environments in ice	CH-473
Beamline :	**Date of experiment :**	**Date of report :**
ID26	from : 12th june 98 to : 15th june 98	24th august 98
Shifts :	**Local contact (s) :**	***Received at ESRF :***
9	Christophe GAUTHIER	01 SEP. 1998

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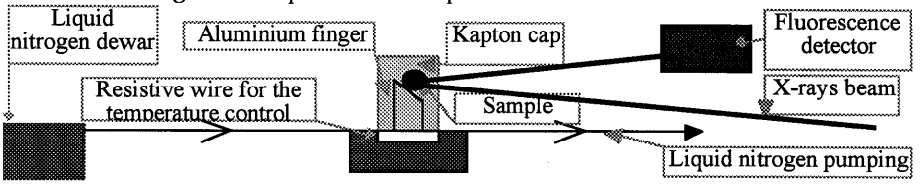
This project had been accepted by the review committee as a comissionning project for ID26. The purpose of our work is to analyze the Br- and Cl- ions environments in ice formed by the rapid freezing of solution : this process called riming, that occurs in clouds, is of prime importance in atmospheric chemistry. During riming, the growth velocity of ice is large so that the solute halogen gases are trapped into ice, in concentrations much higher than the equilibrium solubility. The mechanisms of incorporation, as well as the environment of the halogens in the ice, are not known. The retention structures (depending notably on temperature and on halogens concentration) that may be formed by Br^- or Cl^- are (1) hydrates of HBr (di-,tri- or tetra-hydrate) or of HCl (hexa- or u-i-hydrate), (2) concentrated liquid solutions of HBr or HCl, or (3) solid solutions of HBr or HCl in ice, where the halogens may occupy out of equilibrium sites. In order to identify the true riming retention structure, we first have to determine individually the structure of each possible retention phases. The determination of the liquid solution structures will also be useful to understand the liquid to solid phase transition. Hydrates structures are crystallines and are well known in the literature. On the contrary, the structure of HBr and HCl solutions in function of their concentration has never been analyzed.

During the allocated beamtime of june, we have analyzed the structures of HBr solutions of different concentrations. Numerous spectra were recorded, and we then begun the study of HBr in frozen samples. We did not have time to work with HCl.

Figure 1 : Experimental set-up used on ID26.



The experimental set-up is shown on figure 1. Droplets of HBr solution were deposited at room temperature. The doped rime ice was obtained by supercooling and freezing these

droplets at about -10°C. Br K-edge (13474 eV) absorption spectra were recorded by the fluorescence excitation mode, with a silicium photodiode at 90° of the incident flux direction. The data acquisition of each spectrum took about 40 minutes, with a mean energy step of 1 eV and an energy range of 13250 to 14000 eV. For each sample, spectra were recorded until 2 or 3 of them were identical.

Some of the normalized EXAFS spectra obtained for HBr aqueous solutions of concentrations between 40 % and 48 ppm are given on figure 2. The EXAFS oscillations are largely distinguisable among the absorption baseline, even on the 48 ppm spectrum. Preliminary results obtained for ice are shown also on figure 2 (HBr 200 ppm). Oscillations are distinguisable too, but the baseline is damaged by many diffusion peaks from the ice grains.

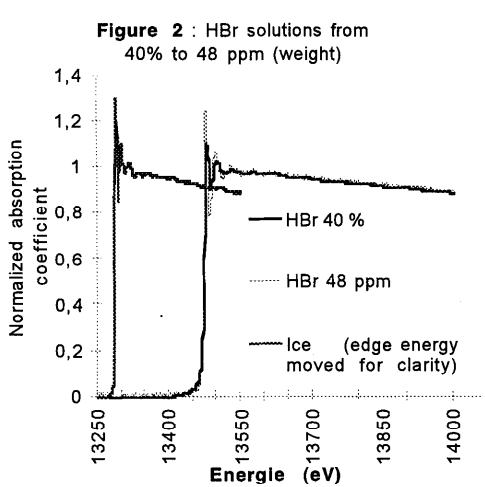


Figure 2 : HBr solutions from 40% to 48 ppm (weight)

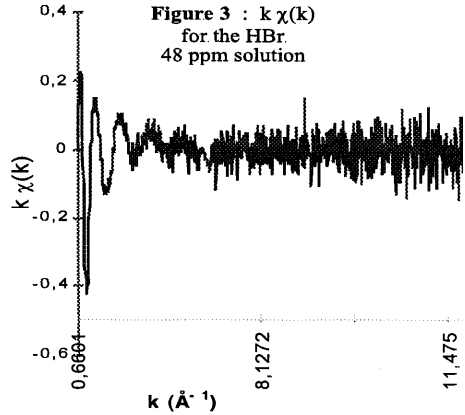


Figure 3 : k χ(k) for the HBr 48 ppm solution

The most important conclusion of these preliminary results is, that since the 48 ppm concentration is close to the atmospheric ones, it is possible to work near real atmospheric conditions and to complete our project successfully on ID26. Furthermore, these results show that the detection limit of ID26 is less than 48 ppm for Br^-, and, considering the literature, we have already reached the lowest concentration analyzed today. Nethertheless, the quality of our spectra has been damaged by a low signal to noise ratio (see figure 3). For the next experiment session in September, much efforts will be taken to reduce the background radiation : use of a selenium filter and of an energy resolving detector. The statistics on the noise will also be improved by modifying the data acquisition mode, for which we will prefer to accumulate numerous quick scans rather than long but few spectra. Finally, the preliminary results on ice show that it is potentially possible to analyze the retention structure of HBr in rime ice, if we delete the problem of diffusion. This will be done by the optical means discussed above, and by an improvement of our sample quality.

Note. We wish to thank C. Gauthier (ID26), as well as V.A. Salt and R. Signorato for their helpful collaboration on the experiment preparation.