THE HCl/H_2O SOLID SYSTEM: INFRARED SPECTRA OF HCl TRI- AND HEXAHYDRATE

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During a long time the assignment of the spectra of the various HCl hydrates, which are known to play an important role in the chemistry of the atmosphere, has been controversial (see the discussions in Refs. [a] and [b]).

In this work we report a joint theoretical and experimental investigation of the vibrational spectra of the crystalline tri- and hexahydrate. The experimental measurements were carried out using grazing angle reflection-absorption IR spectroscopy (RAIRS) on HCl/H_2O samples deposited from the vapour phase and annealed taking into account the appropriate phase diagrams [c]. The theoretical calculations are based on the SIESTA suite of programs [d], a method based on density functional theory and developed for periodic systems of large size. The starting coordinates for the calculation were taken directly from the X-Ray data. After optimisation of the equilibrium geometry of the molecular species within the respective unit cells, the vibrational frequencies corresponding to the normal modes of the crystals were evaluated. From the atomic displacements, an approximate assignment of a given crystal vibration to a combination of molecular modes was possible for frequencies higher than $\approx 1000\ cm^{-1}$. Lower frequencies were seen to correspond mostly to librational crystal modes. Empirical criteria were used for the estimate of the bandwidths corresponding to the various normal modes.

The results of the calculations were compared to the present RAIRS data and to transmission measurements from the literature. The most salient experimental features of the tri- and hexahydrate IR spectra are well reproduced by the theoretical calculations, which allows a theoretical assignment of the observed absorptions.

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