



The HCl/H₂O solid system: infrared spectra of HCl tri- and hexahydrate

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The HCl/H₂O solid system is of great importance in the chemistry of the stratosphere and of the upper troposphere. The uptake of HCl by water ice, the processes of ionisation and solvation, the composition and structure of the possible amorphous and crystalline solids formed, and the heterogeneous chemistry with atmospherically relevant compounds have been the subject of intensive research and present still many open questions (see for instance Ref.[1] and the references therein.)

The highest crystalline hydrates identified in X-Ray measurements contain three and six water molecules respectively. Infrared spectra of HCl/H₂O solids were also recorded, but a long controversy has existed about the assignment of the IR spectra to the various HCl hydrates (see the discussions in Refs.[1,2]), due to the fact that the samples used in the IR and X-Ray experiments are generated by different procedures

In this work we report a joint theoretical and experimental investigation of the vibrational frequencies of the crystalline tri- and hexahydrate. The experimental measurements were carried out using grazing angle reflection-absorption IR spectroscopy (RAIRS) on HCl/H₂O samples deposited from the vapour phase and annealed taking into account the phase diagrams for the stability conditions of the hydrates under consideration [3]. The theoretical calculations are based on the SIESTA suite of programs[4], 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 molecu-

lar 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 $\approx 1000 \text{ cm}^{-1}$. Lower frequencies were seen to correspond mostly to librational crystal 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. The results corroborate and extend previous empirical band assignments with only minor discrepancies. Since the theoretical method is based on a harmonic approximation it has limitations for the description of absorptions associated with strong hydrogen bonds or with various forms of hydrated protons. The relation between the structure and spectra of the two hydrates as well as a discussion of the strengths and disadvantages of the theoretical treatment will be presented at the conference.

1 References

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