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Atmospheric
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Discussions

Interactive comment on "FTIR spectroscopic studies of the simultaneous condensation of HCl and H_2O at 190 K - atmospheric applications" *by* I. Xueref and F. Dominé

Anonymous Referee #2

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Comments on MS 2003-053 by Xueref & Dominé

The paper reports on FTIR work on the H2O-HCl system at 190 K. It is an extension of previous work adding the starting compositions HCl:H2O 5:1, 1:10 and 1:200 to the already published 1:50 case. Due to the high vapour pressures it is not easy to work at temperatures of 190 K, highly relevant to atmospheric conditions, and the authors are apparently the first to succeed. The authors find a very high fractionation of the initial mixtures on solidification close to the composition of HCl hydrates. The experimental work is sound and definitely merits publication. However, some additional issues should be addressed. The finding of the authors that ice Ih turns into an amorphous solid upon doping with HCl is very intriguing. It was essentially obtained

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by comparing the IR-spectra of the different HCl-H2O mixtures to the various forms of ice. While this approach is justified by the circumstances some care must be taken not to over-interpret this finding. It is notoriously difficult to deduce the state of long-range ordering from spectroscopy, a technique which only sensitive to the short-ranged interactions. Diffraction techniques are much better suitable for settling this point. In fact, neutron diffraction work on the HCl-H2O had been recently published (J.Chem.Phys. 116 (2002) 5150) and must be referenced. This work, despite the fact that it is done at different experimental conditions with H2O multilayers on MgO, is lending support the observations made by the authors, both in terms of ice amorphization and the existence of (disordered) hydrates. By quasi-elastic neutron scattering it also shows an enhanced mobility of hydrogen, most likely linked to an enhanced mobility of the water entities. In this context, it may be worthwhile to discuss more explicitly why in contrast to Ritzhaupt & Devlin (1991) no crystallization takes place. In their work the heating of HCl:H2O deposited at low-temperatures produced crystalline hydrates at 175 to 180 K. In fact, the present authors rightly moderate their statements concerning amorphization on p.12 by admitting also an incompletely crystallized phase. Certainly, the obtained phase is not a crystalline hydrate. However, without further evidence it is appropriate at the present stage to emphasize this precaution throughout the paper. In fact, "non-crystalline" is probably the more appropriate term, while the term "amorphous" should be reserved to materials which had been investigated by some diffraction technique. In this context, I do not think that "hydrate" really has a "crystalline connotation" (p.6); like ice also hydrates may be crystalline, badly crystallized or even amorphous. A number of smaller issues should also be listed: (1) on p.4 the used croystat is probably a "closed cycle He-cryostat" working according to the Joule-Thompson principle using compressed He-gas (and not liquid He). (2) On p.7 it may be worth explaining in one sentence why the remarkable CO2 doublets cannot be avoided in the spectra. (3) On p.11 reference is made to the crystalline spectra of the di-hydrate, which is not shown, however. (4) In Fig.4 the individual graphs should be listed in the caption as (a), (b) etc and not a, b- to keep consistency with the other captions. (5) A number of spelling mistakes should be corrected on p.11 line 4 "and", p.12 line 7 eliminate "on", p.14 line 2 "perturb'.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 4037, 2003.