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Interactive comment on “The rate of water vapor evaporation from ice substrates in the presence of HCl and HBr: Implications for the lifetime of atmospheric ice particles” by C. Delval et al.

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This paper reports research that is potentially of considerable value and which has the nice feature of combining mass spectrometric and transmission infrared spectroscopic monitoring of the process. Much related work has suffered from ignorance of the identity of the condensed phase under study. FTIR spectroscopy, particularly using transmission measurements, is an appropriate probe of that identity. (In IRAS, the major bands are so distorted by the combined reflective and absorptive components that the identity of the condensed phase is often dubious; a problem enhanced by the high sensitivity of spectra bandshapes and positions to the angle of incidence and sample thickness.) The cell design described in this paper also seems appropriate to the study

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of HX uptake and reaction with a film of ice; the isolation of the deposition surface (as the only exposed cold surface) being a key feature.

Nevertheless, I reported an unfavorable initial cursory evaluation of this paper and a careful study has not been convincing that the evaluation was wrong. Either this reader is misled by aspects of the paper, or there is a serious fundamental flaw in the measurements. As I understand the spectroscopic experiments (which went hand in hand with the kinetic measurements) a one micron film of ice was first prepared at 180 or 190 K. This film was subsequently exposed to what amounts to a monolayer or less of HX (no more than 10^{15} molecules for slightly less than a square cm of surface). The next step is not completely clear to me. Either the spectra were then scanned to give figures 9-11 or the scanning is done under stirred flow conditions. The latter implies that the film is evaporating. That point is made on page 8 where it is stated that (for Fig. 9 anyway) the spectrum corresponds to the interval B to D of Fig. 3.

It baffles me how a single spectrum such as in Fig. 9 can be considered representative of such an extensive range of film thickness (unless it is a difference spectrum, which is not stated), but this is not the key problem. The problem I find with Fig. 9 and 10 (and presumably Fig. 11) is that the intensity of the hydrate bands (in the range of 0.3 absorbance units), corresponds to a hydrate layer several tenths of a micron thick. Even at a 6/1 water/acid ratio, this would correspond to more than an order of magnitude more HX than the quoted dosage. Where is all this acid coming from?

The happy solution may be that we are not to take the absorbance values of Figs. 9-11 seriously as may be hinted at by the ambiguous statements in the figure captions, i.e., Both traces are rescaled for legibility. If this means the ordinate values do not apply to the acid doped spectra, then it must be said so clearly. The unhappy answer is that the method of estimating dosage level is not working so that all results are suspect. It may be that the cell walls, despite being warm, are alternately taking up and releasing large amounts of acid (and I would surely expect that they would in an otherwise closed system) and that the MS calibration is not adequate to reveal this.

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Given the difficulty level of these experiments it might be well that the system/methods be tested on a somewhat less difficult measurement, such as the same ice-acid components but at a lower temperature (150 - 160 K ?). This might not allow the measurement of relative desorption rates but it would provide hydrate spectra more easily compared to literature spectra and, possibly, values for the rate of acid-hydrate formation in the absence of rapid sample loss.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 2179, 2003.

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