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HO_2NO_2 and HNO_3 in the coastal Antarctic winter night: A "lab-in-the-field" experiment

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Observations of peroxynitric acid (HO_2NO_2) and nitric acid (HNO_3) were made during a 4 month period of Antarctic winter darkness at the coastal Antarctic research station, Halley. Mixing ratios of HNO_3 ranged from instrumental detection limits to 8 parts per trillion by volume (pptv), and of HO_2NO_2 from detection limits to 5 pptv; the average ratio of HNO_3:HO_2NO_2 was 2.0($\pm$0.6):1, with HNO_3 always present at greater mixing ratios than HO_2NO_2 during the winter darkness. An extremely strong association existed for the entire measurement period between mixing ratios of the respective trace gases and temperature: for HO_2NO_2, R^2 = 0.72, and for HNO_3, R^2 = 0.70. We focus on three cases with considerable variation in temperature, where wind speeds were low and constant, such that, with the lack of photochemistry, changes in mixing ratio were likely to be driven by physical mechanisms alone. We derived enthalpies of adsorption (ΔH_{ads}) for these three cases. The average ΔH_{ads} for HNO_3 was -42$\pm$2 kJ.mol^{-1} and for HO_2NO_2 was -56$\pm$1kJ.mol^{-1}; these values are extremely close to those derived in laboratory studies. This exercise demonstrates i) that adsorption to/desorption from the snow pack should be taken into account when addressing budgets of boundary layer HO_2NO_2 and HNO_3 at any snow-covered site, and ii) that Antarctic winter can be used as a natural "laboratory in the field" for testing data on physical exchange mechanisms.