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The absolute absorption cross section of crystalline αg and βg $HNO_3 3H_2O$ (NAT) and $HNO_3 2H_2O$ (NAD) in the range 180 - 200 K in the mid-IR (4000 to 600 cm^{-1})

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Heterogeneous processing in the polar atmosphere requires the presence of polar stratospheric cloud particles (PSC's) that are the seat of interfacial chlorine and NO_x chemistry. A subgroup of PSC's, namely PSC Ia, are known to consist of hydrates of nitric acid, mostly nitric acid trihydrate (NAT) as two polymorphs, α- and β-$HNO_3 3H_2O$ occurring in the range 185 to 200 K under prevailing stratospheric partial pressure conditions of 10 ppb HNO_3 or so. Despite the fact that reference IR spectra in the mid-IR range have been obtained some time ago (Ritzhaupt and Devlin (1991), Koehler et al. (1992)), no absolute absorption cross section of these important ice particles exist to date except a study of its refractive indices (Middlebrook et al. (1994), Berland et al. (1994)). Knowledge of optical cross sections would enable remote sensing of PSC's in the IR region using satellite and/or LIDAR platforms. We have embarked on a multidiagnostic research program aiming at studying the kinetics, thermodynamics and spectroscopy of PSC's using a stirred flow reactor equipped with FTIR absorption spectroscopy in transmission. The gas phase was monitored using electron-impact residual gas mass spectroscopy together with pulsed and steady-state gas admission and thorough characterization of the adsorption of HNO_3, H_2O and HCl onto the stainless-steel vessel walls under mass balance conditions using measured Langmuir adsorption isotherms. We have grown α- and β-NAT by doping thin (1 μm thick) ice films with metered amounts of HNO_3. According to known phase diagrams we have obtained mixtures of pure ice with NAT whose IR spectrum was obtained after spectral subtraction of the pure ice phase. The concentration of HNO_3 deposited on the ice film was determined by measuring the inflow and taking into account adsorption of HNO_3 on the reactor walls as well as effusive loss out the reactor. We also independently checked the H_2O concentration of α-NAT from the decrease of the pure H_2O ice symmetric stretch vibration at 3233 cm^{-1} (ν_1) upon formation of α-NAT. For β-NAT mass balance considerations during the transition from the metastable α-isomer to the stable β-form enables the determination of the HNO_3 concentration in the condensed phase. These results will be discussed in terms of characteristic IR absorptions across the mid-IR range together with corresponding absolute optical absorption cross sections for pure ice and for crystalline $HCl 6H_2O$ recently published (Chiesa and Rossi, (2013)). It turns out that of the three HNO_3 hydrates investigated in this work each has at least one characteristic IR absorption peak enabling unambiguous identification in the presence of the other two and pure ice. Some representative results for the symmetric stretch vibration of H_3O^+ in NAT and NAD are the following: σ(α-NAT, 1760 cm^{-1}) = (6.5 ± 0.3) 10(-19), σ(β-NAT, 1846 cm^{-1}) = (5.6 ± 0.1) 10(-19), σ(NAD, 1676 cm^{-1}) = (1.13 ± 0.08) 10(-18) cm^{2}molec^{-1}.