Infrared optical constants of highly diluted sulfuric acid solution droplets at cirrus temperatures

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Complex refractive indices for supercooled sulfuric acid solution droplets in the mid-infrared spectral regime (wavenumber range 6000 – 800 cm⁻¹) have been retrieved for acid concentrations ranging from 33 to 10 wt% H₂SO₄ at temperatures between 235 and 230 K, from 36 to 15 wt% H₂SO₄ at temperatures between 225 and 219 K, and from 37 to 20 wt% H₂SO₄ at temperatures between 211 and 205 K. These measurements cover for the first time the composition regime which is involved when supercooled H₂SO₄/H₂O solution droplets enter an environment that is supersaturated with respect to the ice phase at temperatures below 235 K. The optical constants were derived with a Mie inversion technique from measured H₂SO₄/H₂O aerosol extinction spectra which were recorded during controlled expansion cooling experiments in the large coolable aerosol chamber AIDA of Forschungszentrum Karlsruhe (Wagner et al., 2008).

The experimental trajectories of these expansion cooling cycles closely follow an atmospheric composition trajectory (Fig. 1). Initially concentrated H₂SO₄/H₂O solution droplets are subjected to a gradually increasing relative humidity upon cooling. Thereby, the sulfuric acid solution droplets continuously dilute until they finally freeze at some threshold composition.

Model calculations of the condensational growth of the sulfuric acid solution droplets were performed with the computer model MAID (Bunz et al., 2008). These calculations demonstrated that the aerosol particles had sufficient time to reach equilibrium with temperature and water vapor to possess a well-defined composition during the expansion cooling cycles. Fast and highly accurate water vapor measurements by means of direct tunable diode laser absorption spectroscopy were used in combination with the Aerosol Inorganics Model (AIM) to infer the composition of the sulfuric acid solution droplets.

The new low-temperature optical constants for highly diluted sulfuric acid droplets reveal significant temperature-induced spectral variations in comparison with the refractive indices for higher temperatures, which are associated with a change in the equilibrium between sulfate and bisulfate ions (Fig. 2).

Figure 1: Experimental trajectories of three expansion cooling experiments with supercooled sulfuric acid solution droplets within the sulfuric acid – water phase diagram. Highlighted by black dots on the trajectories are the specific acid concentrations for which the optical constants were determined (see Fig. 11 in Wagner et al., 2008).

Figure 2: Temperature dependence of the spectrum of the imaginary part of the complex refractive index (k) of H₂SO₄/H₂O for an acid concentration of 25 wt% H₂SO₄ (see Fig. 12 in Wagner et al., 2008)