Investigation of the Photolysis of Nitric Acid on Surfaces by Using Cavity Ring-Down Spectroscopy and Its Novel Variant

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Nitric acid (HNO_3) is a major atmospheric oxidation product of NO_x. Although its gas-phase photolysis in the troposphere is slow, the photolysis rate for HNO_3 deposited on ground and vegetation surfaces to form HONO and NO_x has been reported to be 1-2 orders of magnitude faster than that in the gas phase. The photolysis of HNO_3 adsorbed on ground surfaces has been proposed as a major daytime source of HONO in low-NO_x environments. To understand the difference between the nitric acid photolysis rate in the gas phase and the rate of photolysis on surfaces, my group[1,2] have determined the UV absorption cross sections of HNO_3 adsorbed on fused silica surfaces in the 290-365 nm region by using Brewster angle cavity ring-down technique. Our study showed that the surface absorption cross sections of HNO_3 are at least two orders of magnitude higher than the cross section values of the nitric acid vapor, in the wavelength region studied. We also directly measured the 308 nm absorption cross sections of HNO_3 on Al surfaces and on ice films[3] with a complementary technique, and compared the HNO_3 cross section values on various surfaces. My group have investigated the photolysis of nitric acid on aluminum surfaces,[3] on ice films,[3] and on fused silica surfaces,[4] by using excimer laser photolysis at 308 nm combined with cavity ring-down spectroscopy or with Brewster angle cavity ring-down spectroscopy. We have determined the quantum yields of NO_2^* (electronically-excited NO_2) from the HNO_3 photolysis on aluminum surfaces, on ice films, and on fused silica surfaces, and examined the dependence of the photolysis quantum yields on surface types.

References

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