Supporting Information

Kinetic Isolation of Reaction Intermediates on Ice Surfaces. Precursor States of SO_2 Hydrolysis

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Estimation of the Population of Intermediate Species

The population of the ionic intermediate species on the surface was estimated from LES anion signal intensity. For the calibration of LES intensity, a reference sample was prepared to have a predetermined amount of hydroxide ions on the surface. The hydroxide ions were provided by depositing a known amount of Na atoms on a D_2O-ice film, which produced Na^+ and OD^- ions at 140 K via spontaneous stoichiometric reaction [Kim et al., *J. Phys. Chem. C* **2009**, *113*, 321]. When the reference sample was prepared to have OD^- surface population of 0.2 MLE, LES measurements gave OD^- signal intensity of 510 cps from this surface. To compare, the OD^- intensity in the spectrum of Fig. 1(b) was 110 cps, which corresponded to the "OD^- population" of about 0.04 MLE on the surface. The sample in Fig. 1(b) was prepared by SO_2 exposure of 0.2 L on a D_2O-ice surface at 140 K. We assumed that the OD^- population thus estimated represented the population of intermediates II and III, because these intermediates produced an OD^- signal. The efficiency of OD^- emission could be different for these species and the hydroxide ions externally provided on the reference sample, but probably not to a large extent.

The population of molecular SO_2 adsorbates was estimated from the RIS signal intensity of $CsSO_2^+$. The sample employed in Figure 1 had the initial SO_2 coverage of 0.2 MLE at 100 K, if we assumed that the sticking coefficient of SO_2 was unity on the ice surface at a low temperature. The SO_2 population was reduced by a factor of 10 upon heating the sample from 100 K to 140 K, as shown by the temperature-dependent variation of $CsSO_2^+$ intensity in Figure 2(a). Therefore, after heating the sample from 100 K to 140 K, 10% (0.02 MLE) of the SO_2 adsorbates remained on the surface as molecular SO_2 species (intermediate I). 20% (0.04 MLE) of the adsorbates underwent reactive conversion to intermediates II and III during the heating, and 70% desorbed from the surface. Owing to the assumptions used in the estimations, these percentages may be reliable only in the order of magnitude.