WATER NETWORK-DEPENDENT CHARGE TRANSLOCATION IN THE $NO^+ \cdot (H_2O)_3$ CLUSTERS: AN OLD RIDDLE OF THE IONOSPHERE BRINGS A MICROSCOPIC GROTTHUSS MECHANISM DOWN TO EARTH

RACHAEL RELPH, BEN ELLIOTT, MICHAEL KAMRATH, MARK A. JOHNSON, *Yale University, Department of Chemistry, P.O. Box 208107, New Haven, Connecticut 06520*; ANNE B. MCCOY, *The Ohio State University, Department of Chemistry, 100 West 18th Avenue, Columbus, Ohio 43210*; ALBERT A. VIGGIANO, *Air Force Research Laboratory, Space Vehicles Directorate, Hanscom Air Force Base, Massachusetts 01731*; and ELDON E. FERGUSON, *National Ocean & Atmospheric Administration, Climate Monitoring & Diagnostics Laboratory, Boulder, Colorado 80305*.

The dominant ions in the D-region of the ionosphere are proton hydrates, $H^+ \cdot (H_2O)_n$, which are formed through a complex mechanism involving clustering, and a water network-mediated reaction, $NO^+ \cdot (H_2O)_3 + H_2O \longrightarrow H^+ \cdot (H_2O)_3 + HNO_2$, that proceeds to products only upon addition of the fourth water molecule. The presence of reactive and non-reactive isomers of $NO^+ \cdot (H_2O)_3$ has been invoked to explain the relatively slow rate of HNO_2 formation from the trihydrate. To address this hypothesis, we have employed isomer-selective, pump-probe spectroscopy to determine the infrared signatures of species nominally present in the $NO^+ \cdot (H_2O)_3$ ion packet prepared in a supersonic jet ion source. Indeed two isomers are found to be present. Strong differences in the spectral patterns of the two isomers suggest that they have quite different geometries, which would be consistent with the isomer-specific reactivity model. One of the patterns yields strongly red-shifted activity in the OH stretching region around 2800 cm^{-1}, which is readily explained by the expected behavior of the bridging hydrogen atoms in a chain structure. The motion of these protons is reminiscent of the von Grotthuss mechanism where sequential dissociation and reformation of OH bonds translocates a proton over large distances by passing through a series of small, pairwise exchanges.