MICROWAVE SPECTROSCOPIC INVESTIGATION OF $HNO_3 \cdots (H_2O)_2$

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Nitric acid is an important reactive species in the atmosphere and the study of its hydrates is of considerable interest. We report the observation of the 1:2 complex $HNO_3 \cdots (H_2O)_2$ via Fourier transform microwave spectroscopy. A-type spectra for a total of 18 isotpomers were recorded, including $^{15}N$, and several $H_2^{18}O$ and deuterium containing species. No b-type transitions were found despite calculations predicting a significant dipole moment along the b-principal axis. Spectral splittings observed indicate internal motion of one or both water units within this complex.

The $HNO_3 \cdots (H_2O)_2$ system adopts a cyclic structure in which the second water unit inserts into the weak, secondary hydrogen bond of $HNO_3 \cdots H_2O$, previously studied in our laboratory. The near-linear hydrogen bond between the acidic proton and the closest water unit is 1.632 (16) $\AA$, a contraction of 0.15 $\AA$ relative to $HNO_3 \cdots H_2O$. The $O \cdots O$ distance between the hydroxyl unit of the acid and the closest water unit is 2.625(16)$\AA$. Detailed structural analysis, discussion of internal dynamics, and comparison to *ab initio* calculations[a] will be presented. Structural characterization of $HNO_3 \cdots (H_2O)_2$ will be discussed in the context of proton transfer, as complexes of this nature help answer the fundamental question of how many water molecules are required to ionize a simple mineral acid.

[a] P. R. McCurdy, W. P. Hess, S. S. Xantheas *J. Phys. Chem. A* **106**(33), 7628, (2002).