

MICROWAVE SPECTROSCOPIC INVESTIGATION OF $\text{HNO}_3 \cdots (\text{H}_2\text{O})_2$

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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 $\text{HNO}_3 \cdots (\text{H}_2\text{O})_2$ via Fourier transform microwave spectroscopy. A-type spectra for a total of 18 isotopomers 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 $\text{HNO}_3 \cdots (\text{H}_2\text{O})_2$ system adopts a cyclic structure in which the second water unit inserts into the weak, secondary hydrogen bond of $\text{HNO}_3 \cdots \text{H}_2\text{O}$, previously studied in our laboratory. The near-linear hydrogen bond between the acidic proton and the closest water unit is 1.632 (16) Å, a contraction of 0.15 Å relative to $\text{HNO}_3 \cdots \text{H}_2\text{O}$. The O \cdots O distance between the hydroxyl unit of the acid and the closest water unit is 2.625(16) Å. Detailed structural analysis, discussion of internal dynamics, and comparison to *ab initio* calculations^a will be presented. Structural characterization of $\text{HNO}_3 \cdots (\text{H}_2\text{O})_2$ 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.

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