

## MICROWAVE SPECTRUM OF TRIFLIC ACID DIHYDRATE AND TRIHYDRATE: EVIDENCE FOR COMPLETE PROTON TRANSFER IN A MICROSOLVATED SUPERACID

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Microwave spectra have been observed for the dihydrate and trihydrate of triflic acid ( $\text{CF}_3\text{SO}_3\text{H}-(\text{H}_2\text{O})_2$  and  $\text{CF}_3\text{SO}_3\text{H}-(\text{H}_2\text{O})_3$ ). For the dihydrate, spectra for  $\text{CF}_3^{34}\text{SO}_3\text{H}-(\text{H}_2\text{O})_2$  and  $\text{CF}_3\text{SO}_3\text{H}-(\text{D}_2\text{O})_2$  were also identified. The fitted rotational constants for both the triflic acid dihydrate and trihydrate are in consistently good agreement with those derived from their respective global minimum structures calculated with various DFT methods. The two water molecules in the dihydrate bind to triflic acid in a cyclic arrangement to form an 8-membered ring, resembling an insertion of a second water molecule into the 6-membered ring of the triflic acid monohydrate. For the triflic acid trihydrate, however, rather than form a 10-membered ring via insertion of a third water molecule into the dihydrate geometry, the global minimum structure represents a hydronium triflate ion pair solvated by two water molecules ( $(\text{CF}_3\text{SO}_3^- \text{H}_3\text{O}^+)-(\text{H}_2\text{O})_2$ ). This work represents direct experimental evidence in support of the predicted transition from hydrogen bonding to ion pair formation when triflic acid is solvated with only three water molecules.