TOWARDS THE SOLVATION OF THE PEPTIDE BOND: ROTATIONAL SPECTRUM OF THE WATER-WATER-FORMAMIDE COMPLEX

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Formamide (H_2NCHO), the simplest molecule to contain a peptide linkage, has long served as a test case for the evaluation of computational chemistry algorithms and for the the experimental and theoretical investigation of hydrogen bonding. The rotational spectrum of the complexes of formamide with water and methanol have previously been studied[a], revealing doubly hydrogen-bonded structures with the proton of the water or methanol bonded to the carbonyl oxygen of the formamide and one of the amide protons of the formamide bonded to the oxygen of the water or methanol. Here, we present the first microwave spectrum of the complex between formamide and two water molecules. The observed spectrum is consistent with a rigid complex, having nonzero a- and b-type electric dipole moment components. No c-type transitions are observed, suggesting that c-axis dipole moment component is significantly smaller than the a and b components. The rotational transitions exhibit nuclear quadrupole hyperfine structure from the I = 1, ^{14}N quadrupolar nucleus of the formamide. The sensitivity of these patterns to the rotational quantum numbers validates the rotational assignment. The transitions have been least-squares fit to a asymmetric-rotor nuclear-quadrupole Hamiltonian to determine A = 4384.3387(64) MHz, $B + C$ = 4281.6057(19) MHz, $B - C$ = 979.337(13) MHz, Δ_J = 1.22(32) kHz, Δ_{JK} = 20.68(86) kHz, Δ_K = -17.1(18) kHz, δ_J = 0.431(71) kHz, δ_K = 8.4(22) kHz, eQq_{aa} = 1.0721(39) MHz, and $eQq_{bb} - eQq_{cc}$ = 5.1019(61) MHz. The microwave results are consistent with the *ab initio* calculations of Chen and Gordon[b] which give a triply hydrogen bonded cyclic structure, in which the two water subunits are bonded in a water-dimer-like arrangement.

[a] F.J. Lovas, R.D. Suenram, G.T. Fraser, C.W. Gillies, and J. Zozom, *J. Chem. Phys.*, 88, 722-729 (1988)
[b] W. Chen and M.S. Gordon, *J. Chem. Phys.*, 105 11081-11090 (1996)