ROVIBRATIONAL DYNAMICS OF ORTHOHYDROGEN-WATER COMPLEXES IN SOLID PARAHYDROGEN

MARIO E. FAJARDO, *AFRL/MNME, Energetic Materials Branch, Ordnance Division, U.S. Air Force Research Lab, 2306 Perimeter Rd., Eglin AFB, FL 32542-5910. mario.fajardo@eglin.af.mil.*

Analysis of the rovibrational infrared (IR) absorption spectra of water (H_2O, D_2O) molecules isolated in solid parahydrogen (pH_2) reveals their existence as very slightly hindered rotors, with rotational constants reduced by only 2-5% from their gas phase values. Clustering of residual orthohydrogen (oH_2) molecules with water monomers results in the appearance of several new IR absorption features. For Type B water monomer bands (e.g. ν_1, ν_2) most of the new features appear near the vibrational origin, and were originally interpreted as indicating the presence of "non-rotating" water molecules.[a] However, for Type A bands (e.g. ν_3, $\nu_2 + \nu_3$, $2\nu_2 + \nu_3$, $\nu_1 + \nu_3$) very little IR activity is observed near the vibrational origin, refuting this appealingly simple explanation. Here we propose a new interpretation which assumes a semi-rigid C_{2v} structure for the ground state of the oH_2-water complexes, with the oH_2 acting as a proton donor to the water oxygen atom. In this picture, the oH_2-water complex spectra can be understood as parallel and perpendicular bands of an asymmetric top near the prolate symmetric top limit.[b] Thus, the features bunching near the Type B vibrational band origins arise from the $\Delta K = 0$ selection rule for parallel bands, while the more widely separated features in the Type A bands arise from the $\Delta K = \pm 1$ selection rule for perpendicular bands.

[a] M.E. Fajardo, 57th International Symposium on Molecular Spectroscopy, paper MF01 (2002).

[b] M.E. Fajardo, S. Tam, and M.E. DeRose, J. Mol. Struct. accepted (2004).