

ELECTRIC DIPOLE MOMENTS OF HIGHLY EXCITED VIBRATIONAL STATES OF H₂O: INTERACTION OF ROTATION AND LOCAL MODE TUNNELING.

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We have used LIF-detected, Stark Photofragment Quantum Beat Spectroscopy to measure dipole moments of highly excited vibrational states of H₂O. Unlike the case of HOD discussed in the previous talk, the two bonds in H₂O are equivalent. Hence, the permanent dipole and one of the axes of the vibrationally averaged inertial tensor are always aligned with the molecular symmetry axis. We show that these hypotheses and traditional permanent dipole moment Stark analysis badly fail to model the observed quantum beats, as they do not account for two important characteristics of water. First, the highly excited OH stretching modes of water investigated are best described by properly symmetrized $|n0\pm\rangle$ combinations of local modes, which form an almost degenerate pair. Second, typical separation between rotational states is much larger than the separation between the $|n0\pm\rangle$ pair, that is, rotations occur on a time scale much faster than the tunneling time for local mode excitation to swap bonds. Therefore, the equivalence between the two bonds enforced by the tunneling is dynamically broken on the time-scale of molecular rotation. A simple local-mode rovibrational Hamiltonian [K. K. Lehmann, *J. Chem. Phys.* **95**, 2361 (1991)] correctly accounts for all of the above and provides clear physical insight into the problem.

In addition to providing a stringent test for calculation of dipole moment surfaces, the results presented here have significant implications for the modeling of overtone absorption intensities and lineshapes, and of collisional energy transfer processes involving vibrationally excited water molecules.

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