

VIBRATIONAL ENERGY DEPENDENCE OF THE ELECTRIC DIPOLE MOMENT OF WATER

ANDREA CALLEGARI, PATRICE THEULÉ, and THOMAS RIZZO, *Institut des sciences et ingénierie chimiques, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*; J. S. MUENTER, *Dept. of Chemistry, University of Rochester, Rochester, NY 14627*.

We present a detailed analysis of water dipole moments in highly vibrationally excited states. We use Stark Induced Photofragment Quantum Beat Spectroscopy to measure Stark splittings in vibrationally excited H₂O and HDO, and to obtain the projections of the dipole moment on the rotational inertia axes, μ_a and μ_b , for 7 different vibrational states containing 4, 5 and 8 quanta of O-H stretching excitation^{a,b}. These measurements, combined with earlier studies of $v = 0$ and $v = 1$ states, provide 22 individual dipole moment components in water molecules having vibrational energies extending over a range of 28 000 cm⁻¹.

To understand quantitatively the vibrational dependence of these moments and the origin of their change, we have developed a dipole moment model that accounts for the change of both molecular geometry and electronic charge distribution upon vibrational excitation. In this model, the O–H bond vibration, where the great majority of the excitation is localized, is represented by a Morse oscillator wavefunction; the bond angle is treated parametrically and optimized for each state to reproduce experimental rotational constants; the dipole surface is based on the *ab initio* calculations of Schwenke and Partridge^c. Considerable care is required in the vibrational averaging process to produce calculated moments whose magnitude and orientation can be directly compared with experimental measurements. The results, which are accurate to a few percent, will be discussed in terms of general trends, including the relative importance of stretching vs. bending motions.

^aA. Callegari, P. Theule, T. R. Rizzo and J. S. Muentner, The Ohio State International Symposium on Molecular Spectroscopy, 57th (2002), and 58th (2003)

^bA. Callegari, P. Theule, J. S. Muentner, R. N. Tolchenov, N. Zobov, O. Polyanski, J. Tennyson, and T. R. Rizzo, *Science*, **297**, 993 (2002). P. Theule, A. Callegari, T. R. Rizzo and J. S. Muentner, *J. Chem. Phys.* **122**(13), ppp (2005).

^cD. W. Schwenke, and H. Partridge, *J. Chem. Phys.*, **113**, 6592 (2000).