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 H_2O 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 vibratonal 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.

[a] A. Callegari, P. Theule, T. R. Rizzo and J. S. Muenter, The Ohio State International Symposium on Molecular Spectroscopy, 57th (2002), and 58th (2003)

[b] A. Callegari, P. Theule, J. S. Muenter, 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. Muenter, *J. Chem. Phys* **122(13)**, ppp (2005).

[c] D. W. Schwenke, and H. Partridge, J. Chem. Phys., **113**, 6592 (2000).