STARK PHOTOFRAGMENT QUANTUM BEAT SPECTROSCOPY: THE DIPOLE MOMENT OF HIGHLY VIBRATIONALLY EXCITED WATER ISOTOPOMERS.

PATRICE THEULÉ, ANDREA CALLEGARI[a] and THOMAS R. RIZZO, *Laboratoire de Chimie Physique Moléculaire, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*; JOHN S. MUENTER, *Dept. of Chemistry, University of Rochester, Rochester, NY 14627*.

Dipole moments of vibrationally excited molecules play central roles in most energy transfer processes. In spite of this, experimental measurements have been, with very few exceptions, limited to ground and first excited vibrational states, due to the difficulty of achieving sufficient excited state population for spectroscopic observation of the Stark effect.

We have recently developed a technique that overcomes these difficulties and allows dipole moment measurements on a large class of molecules and excited states. Pulsed laser pump-probe techniques, Stark quantum beat spectroscopy, and photofragment detection are combined in these experiments. In the specific case of water presented here, a 10 ns laser pulse prepares a wavepacket formed by the coherent superposition of Stark-split M states of the rovibrational energy level of interest. After a prescribed time delay, a second laser pulse probes this wavepacket by transferring it to the dissociative $\tilde{A}^1\tilde{B}_1$ electronic surface. A third laser pulse detects the resulting OH fragments by Laser Induced Fluorescence (LIF). The observed LIF signal reflects the time evolution of the wavepacket which, in turn, depends on the applied Stark electric field, the pump-probe delay, and the sought-after dipole moment.

We have used this approach to measure dipole moments of water and singly deuterated water containing 4 and 5 quanta of OH stretching vibration. Further, using a double resonance excitation scheme, we have measured dipole moments of both species having 8 quanta of OH stretching excitation. These states have $\approx 25,000$ cm^{-1} of internal energy, more than halfway to the bond-dissociation limit. The results presented here represent, therefore, a stringent test for dipole moment surfaces, which are routinely employed to calculate large databases of water absorption lines.

Further, this work shows that in the case of HOD the inertial frame rotation with OH excitation plays an important role in the transition dipole moment tilting away from the OH bond, which was previously attributed to electrical anharmonicity alone.

[a]Current address: Institut de Physique de la Matière Condensée, Université de Lausanne, CH-1015 Lausanne, Switzerland