PHOTODISSOCIATION DETECTION OF MICROWAVE TRANSITIONS IN HIGHLY EXCITED VIBRATIONAL STATES: THE DIPOLE MOMENT OF THE (200) STATE OF HOCl

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This paper describes a new spectroscopic technique which uses photodissociation to detect pure rotational transitions in highly excited vibrational energy levels of the ground electronic state. This method has initially been applied to the HOCl molecule, where Stark effect data and a dipole moment measurement have been obtained for a microwave transition in the (200) vibrational state. In this experiment a pulse of infrared radiation excites the first overtone of the OH stretch of HOCl, the (200) $\leftarrow$ (000) transition, populating the $18_{0,18}$ rotational energy level of the (200) state. The $17_{1,17} \leftarrow 18_{0,18}$ pure rotational transition within the (200) state is then induced by a cw microwave source. After a fixed time delay a visible photon excites $17_{1,17}$ in the (200) state to $18_{1,18}$ in the (600) vibrational state, which lies above the dissociation limit and decays to OH and Cl fragments. The sequential absorption of the infrared, microwave and visible photons is detected by monitoring laser induced fluorescence of the OH dissociation fragment. The microwave transition exhibits a line width of 1.8 MHz FWHM and Stark effect measurements on this transition yield an excited state dipole moment of μ_b = 1.518 D. This technique is quite general and can be applied to states up to and exceeding the dissociation threshold of the ground electronic state.