ELECTRIC DIPOLE MOMENTS OF HIGHLY EXCITED VIBRATIONAL STATES.

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Because the electric dipole moment, μ, depends linearly on vibrational excitation over broad energy ranges, it can serve as a useful diagnostic property in situations of extensive state mixing. For example, dipole moment measurements on the separate components of a fractionated spectrum contain valuable information on the vibrational character of the individual eigenstates accessed by the transition. The primary impediment to this kind of analysis is the difficulty of making excited state Stark effect measurements.

In this paper we discuss two recently developed techniques that combine nanosecond laser excitation and detection with high resolution, pure rotational spectroscopy. In the first method, applied to HOCl, the microwave transition occurs after an O-H overtone excitation and is monitored by subsequent photodissociation and LIF detection of the resulting OH radical fragment. We have used this approach to measure dipole moments of the $\mathrm{v_{OH}} = 2$ and $\mathrm{v_{OH}} = 4$ vibrational states. In a second technique, carried out on formaldehyde, the microwave transition and Stark effect measurement again follow overtone excitation, but in this case we detect the change in rotational state by LIF probing of the terminal level using the ${}^1\tilde{A}_2 \leftarrow {}^1\tilde{A}_1$ electronic transition. In the initial application of this procedure, we use the Stark effect on the $1_{11} - 1_{10}$ rotational transition to measure the dipole moment in v=2 of the asymmetric hydrogen stretch, ν_5. Several applications and generalizations of these techniques will be discussed.