EXTENDING ROTATIONAL SPECTROSCOPY TO HIGHLY EXCITED VIBRATIONAL STATES.

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The structural and dynamical properties of high energy vibrational states on ground electronic surfaces play dominant roles in many areas of chemistry. Since rotational spectroscopy is ideally suited to measuring these properties, extending very high resolution methods to high energy states is an important challenge. Spectroscopic methods, such as direct excitation, stimulated emission pumping and stimulated Raman, provide access to high energy states and a variety of spectroscopic methods can be used to detect subsequent rotational transitions. This general approach, which takes the form of multiple, sequential resonances, can be applied to many chemical systems. This paper focuses on excitation of hydrogen stretching states involving fundamentals, overtones, sequential overtones, hot bands, and combination bands deriving intensity from H atom stretches. Experiments carried out both in Rochester and in Tom Rizzo's EPFL laboratory will be reviewed. Following the excitation step(s), high resolution measurements utilizing microwave, radio frequency, or Stark induced quantum beats are carried out. Many different methods have been used to detect the high resolution measurement, including: molecular beam mass spectroscopy, infrared absorption, unimolecular dissociation, vibrationally mediated photodissociation, and laser induced fluorescence. Experiments on HF, HCN, H_2O, HOCl, NH_3, H_2CO, and HCCD will briefly be reviewed to emphasize the broad applicability of this general approach to extending rotational spectroscopy to high energy states.