

VERY HIGH RESOLUTION MEASUREMENTS WITHIN HIGHLY EXCITED STATES ON THE GROUND ELECTRONIC SURFACE.

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

The previous papers are two examples of our recent efforts to develop experimental methods capable of very high resolution measurements within highly excited vibrational states on the ground electronic surface. Small shifts and splittings associated with Stark, Zeeman, hyperfine, and long term dynamical interactions are targets for these techniques. Our general approach can be divided into three phases: (1) excitation, (2) high resolution measurement, and (3) detection. Several different options are available for each phase. Overtone excitation, stimulated emission pumping, and stimulated Raman methods can be used to populate single rotational levels having vibrational energies extending roughly from 3 000 to 30 000 cm⁻¹. Precise measurements within these states can be made with radio frequency, microwave, or quantum beat experiments. The high resolution data can be observed by LIF, unimolecular dissociation, vibrationally mediated photodissociation or REMPI detection techniques. Finally, the molecules under study can be in either low pressure gas or molecular beam samples.

Combinations and permutations of these different approaches provide access to different types of vibrations in a broad range of molecules. We will discuss different configurations for this general type of experiment in terms of sensitivity, resolution, molecular type, and experimental difficulty. Current progress in a number of these areas will be reviewed.

^aCurrent address: Institut de Physique de la Matière Condensée, Université de Lausanne, CH-1015 Lausanne, Switzerland