EVOLUTION OF MOLECULAR ELECTRIC DIPOLE MOMENT UPON VIBRATIONAL EXCITATION.

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Measurements of molecular dipole moments provide important information about the electronic charge distribution in a molecule. Because of the difficulties associated with such measurements, experimental data has so far been limited to ground state and fundamental vibrations. In the past few years we have developed techniques that allow measurement of dipole moments in highly excited vibrational states and used them to study the evolution of molecular dipole moments with vibrational excitation.

Describing the dipole moment change of magnitude and direction upon vibrational excitation involves different contributions, which will be discussed in this presentation, arising from electronic charge redistribution and inertia-frame rotation. The electronic charge distribution can be separated in bond-dipole and electrical anharmonicity contributions both arising from the spatial displacement of charge upon vibration, respectively with and without redistribution of electrons among the atoms. Conversely, inertia-frame rotation is a purely mechanical phenomenon arising from the spatial displacement of mass upon vibration, and consequently a change of orientation of the inertial axis of the molecule. While the latter effect is negligible in most cases, it becomes dominant for molecules with only one heavy atom and two or more light ones. We will exemplify these concepts in the case of H_2O and HOD, for both of which we have measured the dipole moment change upon excitation of 4,5 and 8 quanta of OH stretching vibration. We will also discuss how the inertia-frame rotation participates in determining the spectral intensity of ro-vibrational transitions from the ground state.