THE EXCITING PROPERTIES OF HIGHLY EXCITED MOLECULES

ANDREA CALLEGARI[a], *Laboratoire de Chimie Physique Moléculaire (LCPM), Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.*

Highly excited molecules play a central role in many important fields. Combustion, atmospheric and interstellar chemistry, uni- and bi-molecular reactions are just a few examples where the properties of such molecules are relevant.

Among these properties, the electric dipole moment takes part in both radiative and non radiative energy transfer processes, such as light absorption and collisions, and its knowledge is of fundamental importance whenever these processes occur. Experimental measurements of dipole moments have mostly focused on molecules in their ground or first excited vibrational states, producing a large body of very accurate data. In contrast, only a handful of measurements exist for highly vibrationally excited molecules. This unfortunate situation has its roots in the combined difficulty of preparing highly excited vibrational states and determining with high accuracy the small level splitting induced by an external electric field.

We have developed new techniques to measure the dipole moment of highly vibrationally excited molecules. These techniques are based on a combination of multiple laser overtone excitation schemes with microwave-Stark or quantum beat-Stark measurements. The variety of excitation/detection schemes and Stark methods available makes these techniques quite general and applicable to a vast range of molecules.

The importance of these measurements is well exemplified by the case of water, where the dipole moment surface is used to calculate absorption intensities of atmospheric water vapor. Our measured water dipoles significantly disagree with those calculated from the best available *ab initio* dipole and potential energy surfaces, showing the need for more sophisticated calculations.

[a]Current Address: Institut de Physique de la Matière Condensée, Université de Lausanne, BSP-Dorigny, CH-1015 Lausanne, Switzerland