CALCULATING ROTATIONAL SIGNATURES FOR JAHN-TELLER DISTORTED MOLECULES

KETAN SHARMA, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*; SCOTT M. GARNER, *Department of Chemistry, University of California at Berkeley, Berkeley, CA, USA*; TERRY A. MILLER, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*; JOHN F. STANTON, *Physical Chemistry, University of Florida, Gainesville, FL, USA*.

A Jahn-Teller active molecule demonstrates a characteristic signature in its rotationally resolved spectra due to the distortions from the symmetric configuration. In the past decades, this signature has been used to experimentally access and understand the dynamics around a conical intersection. In this talk we present a method to calculate this rotational signature starting with electronic structure calculations. We derive an Effective Rotational Hamiltonian (ERH) for Jahn-Teller active systems and determine the relationship between the experimentally observable rotational parameters and electronic structure theory. The methodology has been further extended to include molecules with significant spin-orbit interaction. We have calculated both h_1, which manifests from distortions in the plane perpendicular to the highest symmetry rotational axis of the molecule, and h_2, which manifests from out-of-plane distortions of the molecule. We present our findings for cyclopentadienyl (C_5H_5), methoxy (CH_3O) and nitrate (NO_3) radicals and compare them to experimental data available in the literature. These calculations not only help guide experiments but are also a great tool for benchmarking high-level quantum chemistry calculations.