SELECTIVE POPULATION OF MOLECULAR CORE NONPENETRATING RYDBERG STATES

DAVID GRIMES, YAN ZHOU, TIMOTHY J BARNUM, ETHAN KLEIN, ROBERT W FIELD, *Department of Chemistry, MIT, Cambridge, MA, USA*.

Core nonpenetrating Rydberg states of molecules are a neglected state of matter. They could have a variety of uses, notably state-selective production of molecular ions. Due to the $l(l+1)/r^2$ centrifugal barrier that prevents the Rydberg electron in high-l states from penetrating inside of the ion core, the electron is essentially uncoupled from the ion core, and the system becomes atom-like with long lifetimes, an "almost good" l quantum number, and electronic transitions that follow $\Delta J^+=0$ and $\Delta v^+=0$ propensity rules. However, in most molecules access to these states, via a sequence of $\Delta l=+1$ transitions from low-n*, low-l states, is blocked by the necessity to traverse the "zone of death," in which nonradiative decay mechanisms are prohibitively fast. We exploit Chirped Pulse millimeter-Wave (CPmmW) spectroscopy to efficiently excite Ca atoms and BaF molecules to core nonpenetrating states in the absence of nonradiative decay mechanisms. A universal method for preparing core nonpenetrating Rydberg states of molecules, which combines CPmmW spectroscopy with STImulated Raman Adiabatic Passage (STIRAP), will be discussed.