PERTURBATIONS: THE (MODERATELY) HARD WAY TO OBSERVE CORE-NONPENETRATING RYDBERG STATES

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Core-nonpenetrating Rydberg states can provide information about the multipole moments and polarizability of the molecular ion-core. Unfortunately, the nonpenetrating states are not nearly as gregarious as their core-penetrating cousins. The vast majority of known Rydberg states are core-penetrating, and are well characterized precisely because they form regular Rydberg series and have molecular constants very similar to those of the molecular-ion electronic ground state. Nonpenetrating states often appear in fragmentary form as pattern-breakers, borrowing intensity from the penetrating states. As pattern-breakers, they place an enormous burden on spectroscopists, who must assemble the fragments into l-complexes and distinguish the bona fide nonpenetrators from "interlopers" (usually higher-v levels of lower-n penetrating series). CaF and CaCl have very similar electronic structures, but with two important differences: CaCl has a much lower dissociation energy than CaF and CaCl has two Cl isotopes. Vive la difference!

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