“SPECTRUM-ONLY” ASSIGNMENT OF CORE-PENETRATING AND CORE-NONPENETRATING RYDBERG STATES OF CALCIUM MONOFLUORIDE

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Rydberg states of calcium monofluoride in the n*=17–20 region have been observed by ionization-detected optical-optical double resonance spectroscopy via the $D^2\Sigma$ v=1 intermediate state. We describe “spectrum-only” assignment procedures that can be used to assign optical-optical double resonance spectra of core-penetrating and core-nonpenetrating Rydberg states using only information contained in the spectrum rather than predictions derived from an effective Hamiltonian model. Using these methods we have assigned all members of the six core-penetrating Rydberg series and several components of f and g core-nonpenetrating Rydberg states in the n*=17–20 region, and have observed several perturbations between core-penetrating and core-nonpenetrating states. The analysis of these perturbations may enable disentanglement of the dipole, quadrupole, and higher-order ion-core multipole moments.

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