INTERACTION BETWEEN ELECTRONIC AND ROTATIONAL MOTION IN CALCIUM MONOFLUORIDE

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The interplay between electron orbital motion and ion core rotational motion in calcium monofluoride is investigated using multichannel quantum defect theory (MQDT). We illustrate the presence of and alternation between two qualitatively different dynamical regimes in the Rydberg states of CaF: a ″stroboscopic″ regime in which the orbital angular momentum of the Rydberg electron and the rotational angular momentum of the ion core are strongly coupled; and a weak coupling regime in which the two angular momenta are approximately conserved and nearly-pure states of low orbital angular momentum emerge. These results can be understood in terms of the electrostatics of the electron-ion interaction and the classical frequencies of motion of the two particles, and enable us to make general predictions regarding the interaction between electronic and rotational motion in molecules of arbitrary polarity.