We describe experimental and theoretical studies of the effects of resonant electronic state coupling on the formation of ultracold ground-state \(^{85}\text{Rb}_2\). The molecules are formed by photoassociation of ultracold atoms in a MOT into the \(0^+_u\) state converging to the \(5S + 5P_{1/2}\) limit, followed by radiative decay into high vibrational levels of the ground electronic state, \(X^1\Sigma_g^+\). The populations of these high-\(v\) ground-state levels are monitored by resonance-enhanced two-photon ionization (R2PI) through the \(2^1\Sigma_u^+\) state. We find that the populations of vibrational levels \(v'' = 112-116\) are far larger than can be accounted for by the Franck-Condon factors for \(0^+_u \rightarrow X^1\Sigma_g^+\) transitions. Further, the total number of ground-state molecules formed by this process exhibits oscillatory behavior as the PA laser is tuned through a succession of \(0^+_u\) state vibrational levels. Both of these effects are explained by a new calculation of transition amplitudes that includes the resonant character of the spin-orbit coupling between the two states converging to the \(5S + 5P_{1/2}\) limits. The resulting enhancement of more deeply bound ground-state molecule formation will be useful for future experiments on ultracold molecules.

We also describe evidence from our R2PI spectra for extensive singlet-triplet mixing between excited states of \(^{85}\text{Rb}_2\) at intermediate internuclear separations, apparently also induced by spin-orbit interactions. In particular, the \(3^1\Sigma_u^+\) and \(1^1\Delta_g\) states converging to \(5s + 4d\) have been observed in excitation from the \(a^3\Sigma_u^+\) state, and the \(2^2\Pi_u\) state has been observed in excitation from the \(X^1\Sigma_g^+\) state.