We will report experimental results from the pulsed optical-optical double resonance study of Calcium Monofluoride (CaF). These spectra are recorded via D \( ^2\Sigma^+ \) state of CaF in the autoionization region above \( v^+ = 0 \) ionization potential with \( n^* = 15 \sim 45 \). Compared to the OODR spectra of CaCl obtained previously in the same region, more \( ^2\Sigma^+ \) and \( ^2\Pi \) states are assigned for CaF. This can be explained by the predissociation of CaCl. In this autoionization region the disappearance or shift of some members of the predicted CaF core-penetrating series reveals the existence of perturbation between certain states, which is not the case for CaCl. The OODR spectra of CaF in the high-\( n^* \) region indicate that the vibrationally autoionizing states of CaF converge to \( v^+ > 0 \) vibrational levels of CaF\(^+ \) ion. This work completes previous studies of CaF by exploiting different intermediate states, e.g. the reverse-polarized C \(^2\Pi \) state, to investigate the vibrational constant \( \omega_v \) for each Rydberg series and the corresponding quantum defect derivative with respect to the internuclear distance \( R^+ \), which controls the autoionization process.