Higher-ℓ core-nonpenetrating states sample non-roundness of the ion-core through long-range interaction. Higher-ℓ states are not directly accessible, but Stark effect can provide access, through mixing of ℓ. Because of near-degeneracy and exceptionally large transition dipole moments, relatively low fields are required. Unfortunately, owing to strong mixing and high density of states, Rydberg state spectra are hard to interpret, even in absence of the external electric field. In combination with polarization-based diagnostics, we have successfully interpreted Stark effect in double-resonance Rydberg state spectra of CaF in \( n^* = 13 \). Effective Hamiltonian provides a good understanding of how the mixing of ℓ in low-field Stark effect in Rydberg states of CaF occurs. Information about higher-ℓ states can be obtained in a form that is easier to interpret through pure electronic Rydberg spectroscopy, which we are developing. The method benefits from exceptionally large transition dipole moments and employs recent developments in chirped mm-wave and time domain THz technologies.