We report the application of two millimeter-wave detected millimeter-wave–optical double resonance techniques to the study of electronically excited states of CS produced in a pulsed discharge supersonic expansion. In the first technique, millimeter-wave detected millimeter-wave–optical double resonance (mmD-mmODR), the double resonance signal is obtained by monitoring the change in the absorption of resonant millimeter-wave radiation induced by a tunable ultraviolet laser pulse. In the second technique, millimeter-wave polarization-detected millimeter-wave–optical double resonance (mmP-mmODR), polarization-rotation of the resonant millimeter-wave field is used to detect the spatial anisotropy created by the optical resonance. The enhancement in sensitivity achieved by the polarization-labeling technique is used to detect spin-forbidden electronic transitions in CS. We also demonstrate the applicability of these techniques to recording pure rotational spectra of excited electronic states with lifetime-limited resolution.