High resolution excitation spectra have been obtained of the $0-0$ band of the $B^2 A_1 \leftarrow X^2 A_1$ transition of four isotopologues, CaO$^{12}$CH$_3$, CaO$^{13}$CH$_3$, CaO$^{13}$CD$_3$ and CaO$^{15}$CD$_3$ of calcium monomethoxide. The deuterated species were found to have unexpectedly complicated spectra, and definitive rotational assignments were possible only from investigation by optical optical double resonance (OODR) population depletion spectroscopy. This confirmed the assignment of the CaO$^{13}$CD$_3$ spectrum, and proved crucial in assigning the $K$ structure and spin components for CaO$^{13}$CD$_3$. The $B^2 A_1$ state was found to be well described by the symmetric rotor model with $C_{3v}$ symmetry for both hydride species but, for the deuterides, the $K$-structure and spin rotation splittings were irregular, especially for CaO$^{13}$CD$_3$ where the $K = 0$ and 1 levels were heavily perturbed. The results of the OODR experiments will be presented, highlighting the assignment, $K$ structure, spin rotation splitting and perturbations in the $B^2 A_1$ state of the deuterides.