A MO₂ molecule may be in a linear or bent structure. A linear structure could have a D_{∞h} symmetry (OMO, dioxide) or C_{∞v} (MOO, superoxide), whereas a bent structure could have a C_{2v} symmetry (OMO, dioxide; M(O₂), peroxide) or C_{s} (MOO, superoxide). Our spectral and computational analysis shows that MO₂ (M = La) produced in a laser-vaporization cluster beam source has a bent C_{2v} structure in an excited state at the energy of 3.40 eV. The excited state of LaO₂ is \(^{4}B_{2}\) formed by transferring two La electrons to O atoms and has a valence electron configuration consisting of O 2p- and La 6s-based orbitals.