# INVESTIGATING THE EXCITED ELECTRONIC STATES OF BaOH VIA LASER SPECTROSCOPY AND AB INITIO CALCULATION: FURTHER EVIDENCE OF PERTURBATION FROM THE $\tilde{A}'^2\Delta$ STATE

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Two bands for the $\tilde{A}'^2\Delta - \tilde{X}^2\Sigma^+$ transitions of BaOH and BaOD have been rotationally analyzed using high-resolution V-type optical-optical double resonance spectroscopy. BaOH and BaOD molecules were synthesized in a Broida-type oven, using a single mode Ti:Sapphire laser and a single mode dye laser for molecular excitation. The observed spectra mimic a typical $^2\Pi - ^2\Sigma^+$ transition, believed to emanate from single or triple quanta of the bending vibration in the $\tilde{A}'^2\Delta$ state. Measured rotational lines have been assigned and rotational and fine structure parameters determined through a combined least-squares fit with the millimeter-wave pure rotational data of the $\tilde{X}^2\Sigma^+$ state. Previous analyses of the $\tilde{A}^2\Pi - \tilde{X}^2\Sigma^+$ transitions of BaOH and BaOD yielded significantly different spin-orbit coupling constants, which were attributed to possible global and local perturbations arising from vibrationally excited bands of the $\tilde{A}'^2\Delta$ state. Although the newly observed $\tilde{A}'^2\Delta$ state bands could not be conclusively designated a specific spin state, the derived $\Lambda$-doubling constants also show significant $^2\Pi$ character, further indicating a strong interaction between the $\tilde{A}^2\Pi$ and $\tilde{A}'^2\Delta$ states of BaOH. To validate these conclusions, *ab initio* calculations have been carried out to further understand the nature of the BaOH excited states. The wavefunctions of the $\tilde{D}'^2\Sigma^+$, $\tilde{D}^2\Sigma^+$, $\tilde{C}^2\Pi$, $\tilde{B}^2\Sigma^+$, $\tilde{A}^2\Pi$, $\tilde{A}'^2\Delta$ and $\tilde{X}^2\Sigma^+$ states have been optimised with a state averaged multiconfigurational calculation using the MolPro software. Calculated vertical term energies show relatively good agreement with existing optical data.