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

J. D. TANDY, J.-G. WANG, P. F. BERNATH, Department of Chemistry, University of York, Heslington, York,
YO10 5DD, UK; J. LIÉVIN, Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles,
Cpi 1600/09, 50 av F.D. Roosevelt, B-1050 Bruxelles, Belgium.

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 A-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.