

1 *Ab initio* calculations of the O1s XPS spectra of ZnO and Zn oxo 1 compounds

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O1s core level binding energies of oxygen atoms in bulk ZnO, at different ZnO surfaces, and in some Zn oxo compounds were calculated by means of wave function based quantum chemical *ab initio* methods. Initial and final state effects were obtained by Koopmans' theorem and at the Δ SCF level, respectively. After correction for scalar relativistic effects and electron correlation, the
15 calculated XPS peak positions are in excellent agreement with the available experimental data for all systems included in the present study. The O1s core level shifts between an isolated H₂O molecule and the Zn oxo compounds or ZnO, as well as between oxygen atoms in bulk ZnO and at various ZnO surfaces, can be understood by means of Madelung potentials and electronic
20 relaxation or screening. XPS spectra were calculated for various cluster models which are designed to describe different possibilities of stabilizing the polar O-terminated ZnO(000 $\bar{1}$) surface by the adsorption of H atoms. The experimental spectra are only compatible with the theoretical
Q2 results for the fully hydroxylated H-ZnO(000 $\bar{1}$) surface exhibiting a (1 \times 1) surface structure.

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