Ab initio calculations of the O1s XPS spectra of ZnO and Zn oxo 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 ΔSCF level, respectively. After correction for scalar relativistic effects and electron correlation, the 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 H_2O 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 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 results for the fully hydroxylated H–ZnO(000$\bar{1}$) surface exhibiting a (1 × 1) surface structure.