Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Operando XANES from first-principles and its application to iridium oxide

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Electronic Supplementary Information

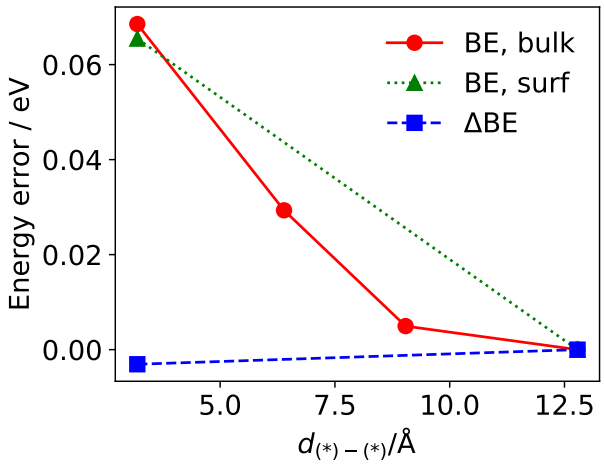

Figure S1: The convergence of the O 1*s* core-electron binding energies (BE's) is investigated as a function of the minimum distance between periodic replicas of the core-excited atom. Absolute binding energies for bulk (BE_{bulk}, red) and surface (BE_{surf}, green) atoms are considered, as well as the relative binding energy: $\Delta BE = BE_{surf}$ - BE_{bulk}. A (110) slab has been employed for the convergence test.

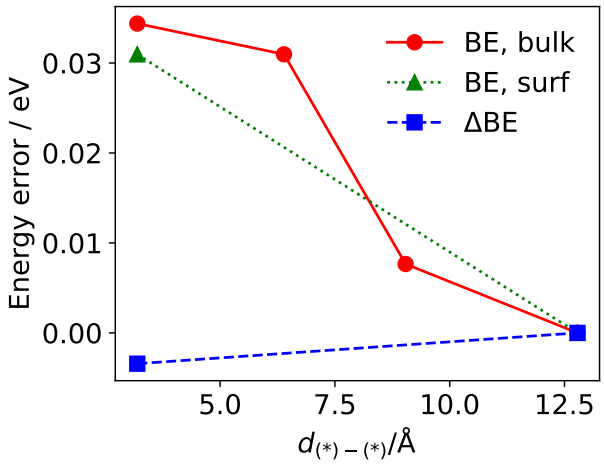

Figure S2: Same as Figure S1, but the Ir 2*p* core-electron BE's are considered instead.

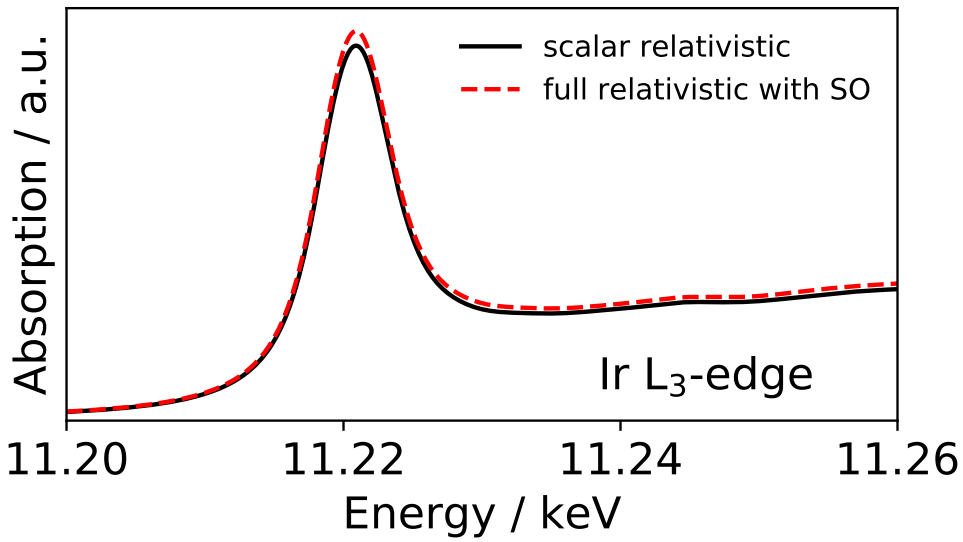

Figure S3: The Ir L_3-edge absorption cross-section computed using as initial state the $2p$ reconstructed all-electron wave function determined using scalar relativistic calculations (solid black) is compared to the cross-section computed using the $2p_{\frac{3}{2}}$ core state from full relativistic calculations that accounts for spin-orbit (SO) coupling (dashed red). Bulk IrO_2 has been employed for the test.

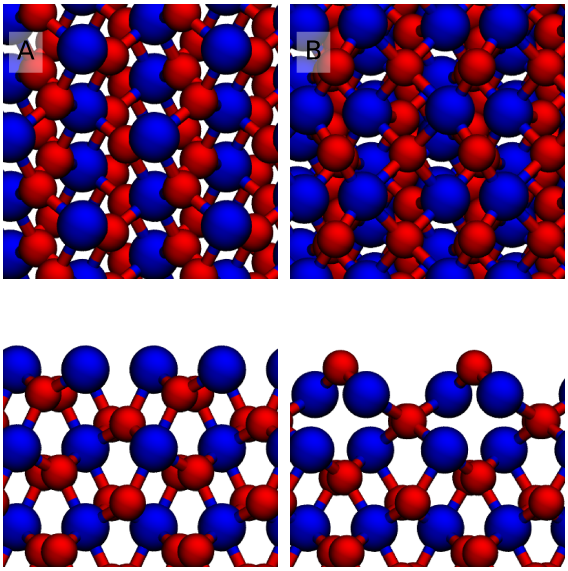

Figure S4: Top and side views of the considered Ir-rich (101) termination. Blue and red balls represent iridium and oxygen atoms, respectively. The two panels on the left (A) illustrate the bulk-truncated structure, while the reconstructed termination is sketched in the right panels (B).

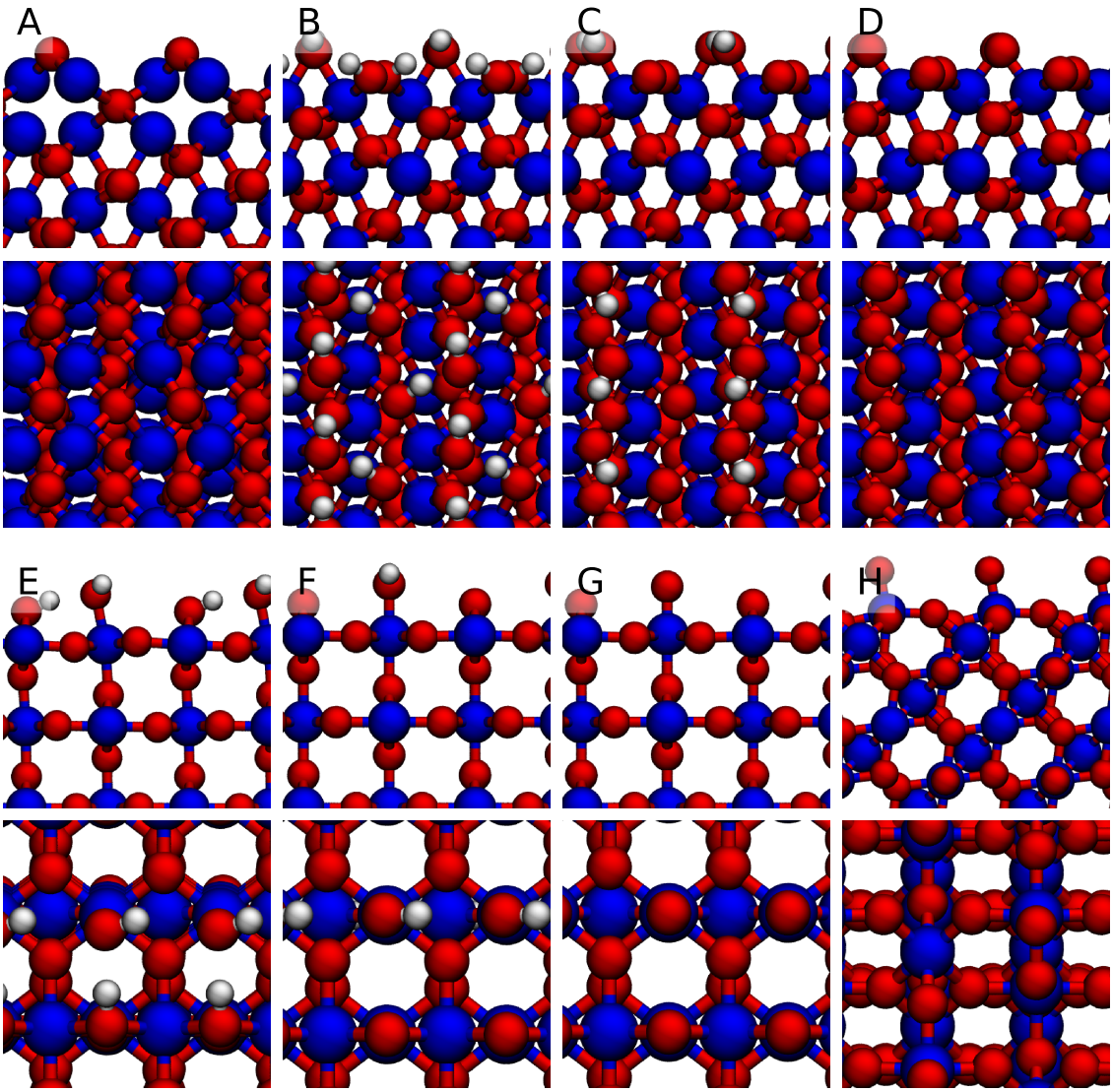

Figure S5: Top and side views of all interfaces for which XANES cross sections have been computed. (A-D): interfaces from the (101) orientation, i.e. the reconstructed iridium-rich surface (A), the OH-covered surface (B), the termination with OH groups at coordinatively-unsaturated (CU) sites (C), and the fully deprotonated surface (D). (E-G): interfaces from the (110) orientation, i.e. the OH-covered surface (E), the termination with OH groups at CU sites (F), and the fully deprotonated surface (G). (H): interface from the (111) orientation, i.e. the surface with an O atom adsorbed at the CU site. The coloring of atoms is as in Figure S4.

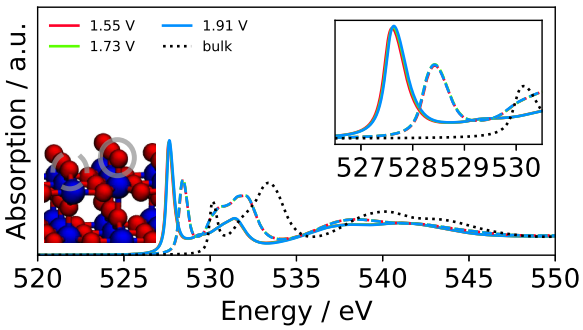

Figure S6: Oxygen K-edge XANES cross sections computed for the fully-oxidized (110) surface. A sketch of the termination is presented in the inset on the left, with blue and red balls indicating iridium and oxygen atoms, respectively. The absorbing atoms are highlighted with a grey circle. The insets on the right include a magnification of the white-line peak region. The various colors identify different potential conditions (curves are to a large extend superimposed).

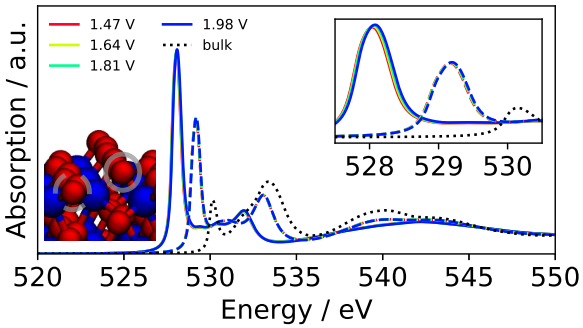

Figure S7: Same as Figure S6, but the absorbing atoms are selected from the fully-oxidized (101) surface.

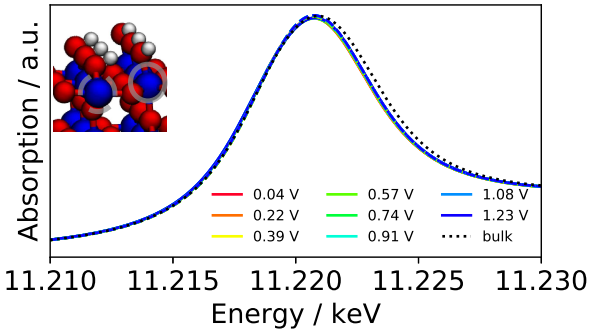

Figure S8: Iridium L_3-edge XANES cross sections computed for the indicated absorbing atoms of the OH-covered (110) surface. The various colors identify different potential conditions (curves are to a large extend superimposed).

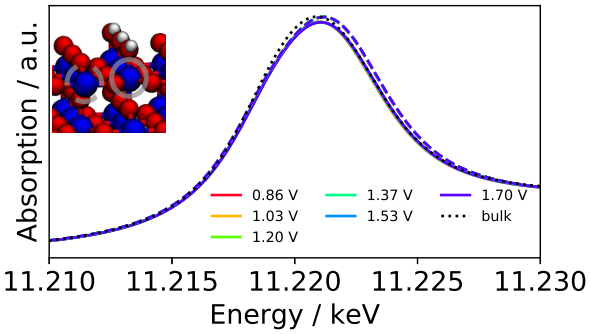

Figure S9: Same as Figure S8, but the absorbing atoms are selected from a (110) termination with OH groups at the CU sites.

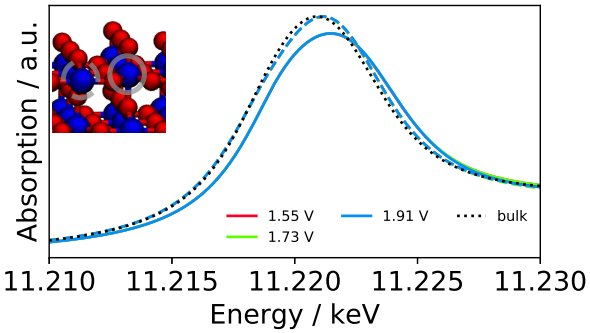

Figure S10: Same as Figure S8, but the absorbing atoms are selected from the fully-oxidized (110) surface.

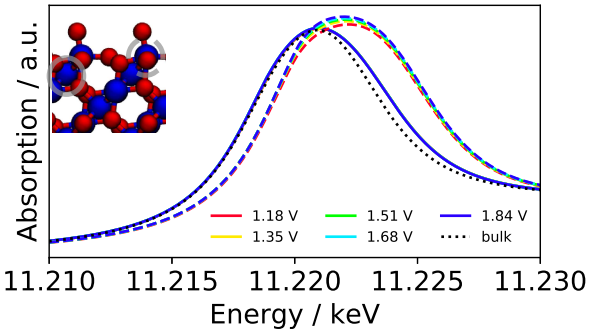

Figure S11: Same as Figure S8, but the absorbing atoms are selected from a (111) termination with an oxygen atom adsorbed at the CU site.